Metastability in statistical mechanics.

Thesis

UNRESTRICTED

METASTABILITY IN STATISTICAL MECHANICS.

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Date of submission 1·3·80
Date of award 26·3·82

Mathematical Physics February, 1980.

ABSTRACT. In this dissertation we deal mainly with the problem of metastability in statistical mechanics. In Chapter I we review the analytic aspects of metastability. Taking stability as the basic concept Sewell defined metastable states to be those states which are locally but not globally stable. For a hard core continuous system the pressure functions of the metastable state is found to be the real analytic continuation in the chemical potential of the pressure for the equilibrium phase In Section 2 we present the result of Landford and Ruelle showing the impossibility, in a model with short range forces, of the existence of metastable states. Langer's method using the Mayer series expansion ends this section. We also discuss two descriptions of metastability based on eigenvalue degeneracy.

In Chapter II we describe the dynamic aspects of metastability. A "restricted ensemble" is defined and it is proved that the escape rate can be made very small. By using the Becker-Döring set of equations it is shown that the behaviour of the system is governed by a "slow mechanism" if the state is a point in the restricted ensemble. We provide a rigorous version of the Boltzmann-factor approximation to the expected number of N-particle clusters m_N. Similar results are shown to hold in a special case of an Ising model and in a hard core continuous model.

In Chapter III we work with a continuous model and obtain an approximation to m_N which is equivalent to the one obtained in Chapter II; by making reasonable assumptions we present an expression for m_N in agreement with the results of nucleation theory.

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INTRODUCTION

One of the outstanding problems in statistical mechanics is the rigorous description of metastable states. The problem arises in a wide variety of contexts and in order to summarize the essential features we shall present the following systems which are known to posses states falling under the category of being metastable.

Fig. I.1 shows the standar form, in the Van der Waals-Maxwell theory, of isothermal below the cririca temperature .

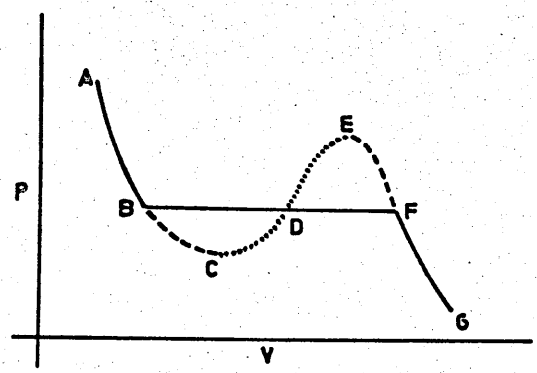


Fig. I.1 The full curve represents the stable states, the broken curve those states that are metastable, and the dotted curve the unstable states.

The stable equilibrium state corresponds to the continuous line ABCDFG with the horizontal line (Maxwell's construction) BD drawn so as to make the areas BCD, and DEF equal. However, if the vapor phase is suppressed the liquid phase AB can be continued as a metastable extension as far as E where it ceases to be stable. Points C and E trace out "spinodal lines" when the temperature is altered.

The magnetic analogue of this phenomenon is illustrated in Fig. I.2 with the magnetic field instead of the pressure and the magnetization instead of the density. It is instructive to look at the above picture in terms of the Helmholtz free energy as a function of magnetization. The stable phase corresponds to the "two tangent line" BF and the spinodal line to points of inflection..

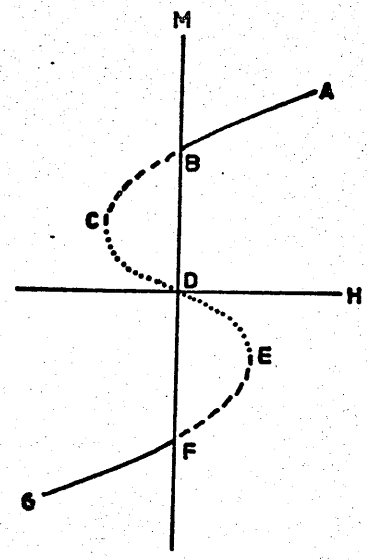


Fig. I.2 Stable and metastable states in the classical picture of a ferromagnet. The states correspond to:
full curve, stable;
broken curve, metastable;
dotted curve, unstable.

If we turn back to the liquid-vapor transition as studied in the Van der Waals-Maxwell theory we see that the graph relating the Helmholtz free enrgy per unit volume to the density looks the same as the graph in Fig. I.3 with the density playing the role of independent variable.

These graphs suggest that underlying these phenomena there must be something common to not only these processes but to a whole variety. The purpose of this thesis is to review the attempts taken in order to build a rigorous theory of metastability. Such theory should describe, once defined what a me-

tastable state, how the state is reached and how it decays. This decay takes place by means of the nucleation and growth of some characteristic disturbance within the metastable system.

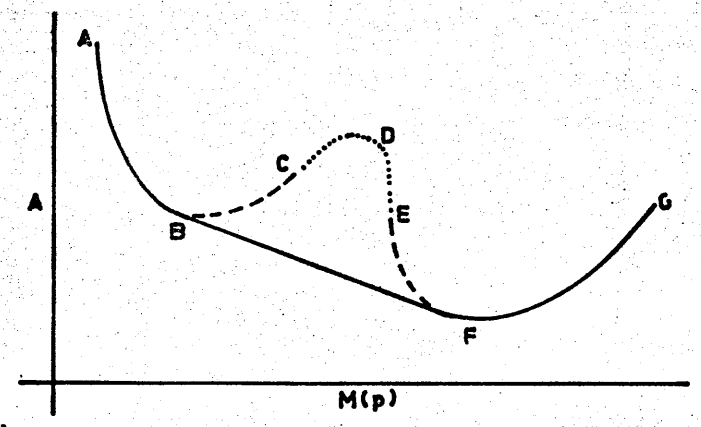


Fig. I.3 Helmholtz free energy of a classical ferromagnet (or fluid) . The states correspond to : full curve, stabe; broken curve, metastable; dotted curve,unstable.

Figs. I.2 and I.3 suggest a metastable state can be described in terms of thermodynamic functions obtained from the extrapolation of the nearby stable states. The problem remains in justifying that such extrapolation can be made and that it describes metastable states. The analytic aspects of the theory are reviewed in Chapter I.

But metastability is the manifestation of a dynamic phenomenon and the static methods described in Chapter I fail to account for features like spinodal decomposition and the rate of decay from the metastable state. In Section 1 of Chapter II we deal with a dynamic description of a lattice gas

whose particles were assumed to obey the Kawasaky dynamics. In Section 2 , and following the method of Penrose and Lebowitz used in the preceding section , we see how the existence of metastable states was proved, firstly on an Ising spin system and secondly on a continuous model. In both cases Minlos and Sinai's technique for defining clusters is used along with the assumption that a master equation governs the dynamics of the system.

In Chapter III we work with a continuous model and obtain an approximation to the expected number of N-particle clusters (m_N) which is formally equivalent to the one obtained by Penrose and Lebowitz for the lattice gas. This expression is in agreement with the one used in nucleation theory if we assume the replacement factor Γ to be equal to m_1^{-1}. That such result is obtained gives support to the idea that, at low densities, Γ should equal m_1^{-1}.

ANALITIC ASPECTS OF METASTABILITY

Section 1: STABILITY

Starting with the obvious demand that thermodynamics must apply to metastable states, these are defined as those states whose free energy exceeds the corresponding minimum value determined by the existing physical constraints.

A formalism that basically is different from the one developed by Penrose and Lebowitz[10,30] has been introduced by Sewell in a series of papers where stability is the property that will characterize metastable states[3,24]. Such approach is more profound than what it seems at first glance. It implies using tha algebraic approach to statistical mechanics and this ultimately means moving along a path intended to put the theory under solid mathematical foundations.

Stability can claim a place of its own in the description of physical phenomena in general and with a particular importance when departures from equilibrium is the subject.This happens because even though we can construct aesthetically beautiful theories they mainly reproduce highly idealized situations inasmuch only non-changing dynamical laws are beingused. It is a fact that alterations to the dynamical law during experimentation will come from the presence of contamination as well as from our imperfect knowledge of the law; thus, in order to allow for experimental reproducibility we can not remain restricted to theories that break under slight modifications of the dynamics. Of course we do not expect them to remain unchanged for a perturbation that is too strong or global in character, or if it takes place while the parameters take values associated to phase transitions. In view of this we shall

deal only with local and infinitesimal changes to the dynamical law.

It might be thought that physical intuition is the only reason why stability appears in the theory, but the striking fact is that it also plays a role in uniquely defining the equilibrium states of the systems, singling out among the possible solutions the one with the special property of being a Gibbs measure[4,5,6,7]. This is important since if somehow metastability can be related to Gibbs states this will provide a great deal of the desired coherence within the framework of statistical mechanics as a general theory describing both the equilibrium and the non-equilibrium situations.

GLOBAL AND LOCAL STABILITY

The first step taken by Sewell in describing metastability was to consider a caracterization of equilibrium states in terms of a variational principle involving the free energy of the system[2,3,12,13]. In what follows preference will be given to the ideas defining our idealized physical system and the method to deal with its description; since rigour in the mathematical apparatus can obscure the treatement, by deviating the attention, it will not be fully exposed keeping the references as the best sources of information about this aspect of the theory.

The system under treatement is the Van der Waals fluid[8,9,10,11], a classical hard core continuos system.

I will keep the notation used in Sewell's article [3].

Let $\mathbb{R}$, $\mathbb{Z}$, $\mathbb{R}_+$, $\mathbb{Z}_+$, $\mathbb{C}$ denote the usual sets, namely the real line, integers, positive reals, pos. integers and the complex plane respectively.

Σ is an assembly of mutually interacting identical classical particles (with hard cores) in T (an Euclidean space).

X is the set of partcle configurations for Σ, ie.

$$X \equiv \{ x \in \mathcal{P}(T) \mid d(t,t') \geq b \ , \ \forall t, t' (\neq t) \in x \}$$

where $\mathcal{P}(t)$ is the family of subsets of T, d the Euclidean metric and b the hard core diameter.

If A (or B) stands for the bounded open (or closed) subsets of T and

$$\Delta_{\alpha n} = \{ x \in X \mid N(x \cap \alpha) \geq n \}$$

$$\Delta_{\beta n} = \{ x \in X \mid N(x \cap \beta) \leq n \}$$

then X will be equipped with the topology generated by the subsets

$$\{ \Delta_{\alpha n}, \Delta_{\beta n} \mid \alpha \in A, \beta \in B, n \in \mathbb{Z}_+ \}$$

The state space Ω of Σ is the set of Radon probability measures on X and Ω_T will stand for the set of translationally invariant elements of Ω.

If $\forall \alpha \in A$ X_α (or X_{α_c}) is defined to be

$$\{ x \in X \mid x \subset \alpha \ (\text{or } \alpha_c) \} \ .$$

then for each $\omega \in \Omega$ there is a Radon probability measure ω_α

(or ω_{α_c}) defined on $\mathfrak{X}_\alpha$ (or $\mathfrak{X}_{\alpha_c}$) by

$$\omega_\alpha(f_\alpha) = \int f_\alpha(x \cap \alpha)\, d\omega(x) \qquad \forall f_\alpha \in \zeta(X_\alpha)$$

with the obvious substitutions for $\omega_{\alpha_c}(f_{\alpha_c})$. Here $\zeta(X_\alpha)$ is the set of all real valued bounded continuous functions on X_α.

Let ϕ be a translationally invariant interaction. Two sets of such interactions will be used, each set defined in terms of the norm its members satisfy:

$$\phi \in \underline{\Phi} \text{ if } \|\phi\| = \sup_{x \in X} \sum_{0 \in y \subset x} |\phi(y)|/N(y) < \infty$$

$$\phi \in \underline{\Phi}_1 \text{ if } \|\phi\|_1 = \sup_{x \in X} \sum |\phi(y)| < \infty \quad \text{for } \phi \in \underline{\Phi} \cap \zeta(Y)$$

The hamiltonian function will then be given by

$$H_\alpha^\phi : X_\alpha \to \mathbb{R} \qquad H_\alpha^\phi(x_\alpha) = \sum_{y \subset x_\alpha} \phi(y)$$

in terms of which the energy density functional $\mu^\phi : \Omega_T \to \mathbb{R}$ can be defined as

$$\mu^\phi(\omega) = \lim_{\alpha \to \infty} (1/|\alpha|) \int H_\alpha^\phi \, d\omega_\alpha$$

with the limit taken in Fisher's sense[14,15].

By analogy to the well known thermodynamical expression, the free energy density functional $f_\theta^\phi : \Omega_T \to \mathbb{R}$ at temperature θ will be given by

$$f_\theta^\phi = \mu^\phi - \theta s$$

where $s : \Omega_T \to \mathbb{R} \cup \{-\infty\}$ is the entropy density functional

$$s(\omega) = \lim_{\alpha \to \infty} \frac{S_\alpha(\omega)}{|\alpha|}$$

where $|\alpha|$ is the Lebesgue measure of α, the limit is taken in Fisher's sense and S_α is the entropy functional $S_\alpha : \Omega \to \mathbb{R} \cup \{-\infty\}$ given by

$$S_\alpha(\omega) = \begin{cases} -k \int \omega_\alpha^{(1)}(x_\alpha) \ln \omega_\alpha^{(1)}(x_\alpha) \, dx_\alpha & \text{if } \omega \in \Omega^{(\alpha)} \\ -\infty & \text{otherwise} \end{cases}$$

In here $\omega_\alpha^{(1)}$ stands for the Radon derivative(69)

In sum, it can be said the free energy density f_θ^ϕ of the closed system is defined as the infinite volume limit of that induced by ω on a finite closed system of mutually interacting particles.

Since global stability is a property associated with the system as a whole it seems, intuitively at least, that any of its characterizations will have to be given in terms of averages or infinite volume limits of particular quantities. The way f_θ^ϕ was defined makes it fit this condition and so it can be related or used to describe global properties of the system.

With thermodynamics as source of inspiration the states of interest will be given in terms of a variational principle involving f_θ^ϕ. More precisely, let $\phi \in \underline{\Phi}_{sc}$ ($\equiv$ the set of $\phi \in \underline{\Phi}$ such that μ^ϕ, hence f_θ^ϕ is lower semicontinuous), $\mathcal{X}^\circ$ a closed subspace stable under translations and

$$\Omega^\circ \text{ (or } \Omega_T^\circ) = \{\omega \in \Omega \text{ (or } \Omega_T) \mid \text{supp } \omega \subset X^\circ\}$$

then

Definition S1 The set $K_G(\theta,\phi)$ (or $k_G^\circ(\theta,\phi)$) of globally stable (or globally X°-stable) translationally invariant states of Σ corresponding to the interaction ϕ and temperature θ is the set of $\omega \in \Omega_T$ (or Ω_T°) that absolutely minimize f_θ^ϕ (or $f_{\theta/\Omega_T^\circ}^\phi$).

Keeping this way of thinking leads us to define local stability in terms of properties depending only on a region surrounding the point in question.

A succesful formalization consisted in taking the class of potentials Φ_2 which make the interaction energy $\tilde{H}_\alpha^\phi$ (on $\tilde{X}_\alpha$) satisfy certain convergence conditions[2]. In here $\tilde{X}_\alpha$[(*)] stands for the joint configuration in X_α and X_{α_c}, ie. $\tilde{X}_\alpha = \{(x_\alpha, x_{\alpha_c}) \mid x_\alpha \cup x_{\alpha_c} \in X\}$ and hence $\tilde{H}_\alpha^\phi$ is the energy due to the particles in α interacting with one another and with the recervoir.

Given the conditional energy functional defined on by $\tilde{U}_\alpha^\phi : \Omega \to \mathbb{R}$

$$\tilde{U}_\alpha^\phi(\omega) = \int \tilde{H}_\alpha^\phi(x \cap \alpha \mid x \cap \alpha_c)\, d\omega_\alpha \qquad \forall \omega \in \Omega,\ \phi \in \Phi_2,\ \alpha \in A$$

(*) The $\sim$ symbol on top of X means we are dealing with conditional configurations, ie. configuration x_α on α given that outside α the configuration is x_{α_c}.

Then the conditional free energy functional $\tilde{F}^{\phi}_{\alpha\theta} : \Omega \to \mathbb{R} \cup \{\infty\}$ corresponding to the temperature θ will be

$$\tilde{F}^{\phi}_{\alpha\theta} = \tilde{U}^{\phi}_{\alpha} - \theta \tilde{S}_{\alpha}$$

where $\tilde{S}_{\alpha}$ is the conditional entropy functional $\tilde{S}_{\alpha} : \Omega \to \mathbb{R} \cup \{-\infty\}$

$$\tilde{S}_{\alpha}(\omega) = \begin{cases} -k \int \tilde{\omega}^{(1)}(x_\alpha | x_{\alpha_c}) \ln \tilde{\omega}^{(1)}_{\alpha}(x_\alpha | x_{\alpha_c}) \, dx_\alpha \, d\omega_{\alpha_c}(x_{\alpha_c}) & \text{if } \omega \in \tilde{\Omega}^{(\alpha)} \\ -\infty \quad \text{otherwise} \end{cases}$$

Obviously $\tilde{F}^{\phi}_{\alpha\theta}$ is local in character and provides the material to define, for $\phi \in \mathcal{F}_2$ the set

Definition S II ... $K_L(\theta, \phi)$ of locally stable sets of $\mathcal{L}$ at temperature θ as those $\omega \in \Omega$ such that

$$\tilde{F}^{\phi}_{\alpha\theta}(\omega) \leq \tilde{F}^{\phi}_{\alpha\theta}(\omega') \qquad \forall \alpha \in A$$

and all states ω' for which $\omega'_{\alpha_c} = \omega_{\alpha_c}$.

For $\phi \in \mathcal{F}_1$, $K_L(\theta, \phi)$ happens to coincide with the set of ω such that $\omega \in \tilde{\Omega}^{(\alpha)}$ and

$$\tilde{\omega}^{(1)}_{\alpha}(x_\alpha | x_{\alpha_c}) = \exp\left[-H^{\phi}_{\alpha}(x_\alpha | x_{\alpha_c})/kT\right] \Big/ \int dx_\alpha \exp\left[-H^{\phi}_{\alpha}(x_\alpha | x_{\alpha_c})/kT\right]$$

which is the same as saying the ω's satisfy the Dobrushin-Lanford-Ruelle (DLR from now on) conditions[16,17]. According to reference (16) the states satisfying the DLR conditions are the equilibrium states for the system. In Sewell's treatment this is not so; the reason is that in this case equilibrium states are supposed to satisfy the global stability condition and it can be proved that for certain systems with $\phi \in \mathcal{F}_{sc} \cap \mathcal{F}_2$ there will be translationally invariant sates ω which are not globally stable, even though $\omega \in K_L(\theta, \phi)$.

Restricting therefore the interaction potentials ϕ to those ϕ's such that $\phi \in \Phi_{sc} \cap \Phi_2$ the following definition seemed appropriate

Definition S III The set of translationally invariant equilibrium states $K_E(\theta, \phi)$ of Σ, corresponding to the ordered pair (θ, ϕ) is $K_G^\circ(\theta,\phi) \cap K_L(\theta,\phi) / K_G(\theta,\phi)$.

In addition, and by reasons that will be justified a-posteriori, a picture of metastability was given by Sewell by defining

Definition S IV ... $K_M^\circ(\theta,\phi)$ to be the set of translationally invariant Σ°-metastable states of Σ corresponding to (θ,ϕ), and defined as identical to

$$K_G^\circ(\theta,\phi) \cap K_L(\theta,\phi) / K_G(\theta,\phi)$$

So defined the Σ°-metastable states possess a free energy whose value exceeds that of the equilibrium state. What is left is to show they have the equilibrium like properties expressed by

Eq. L. Prop. i) Thermodynamical properties for quasi-static transitions.

ii) The preasure is a real analytic continuation in the chemical potential, of that of some true equilibrium phase. (This is a desirable although not a necessary condition).

iii) Very long lifetime.

That definition Def. S IV is a viable one for metastability can be supported, one might say justified, by the ex-

istence of systems whose $K^{\circ}_{\mu}(\theta,\phi)$ states reproduce the behaviour expressed in properties Eq.L.Prop. i),ii) and iii) . An example is provided by the so called mean field theories[18] of which those with a Van der Waals interaction are a particular case.

By a mean field system $\hat{\Sigma}$ (*) is understood an assembly of identical particles with exactly the same characteristics as Σ ,except that the interaction potential will be expressed by

$$\phi_\omega = \phi - g\mu^{\psi}(\omega)\,\psi \qquad (I.1)$$

$\forall\, \omega \in \xi(\Omega_T)$ (where $\xi(\Omega_T)$ is the set of the spatially ergodic states) $\phi \in \Phi_1$, $g \in \mathbb{R}^+$ and $\psi(y)=\delta_{1,N(y)}\ \forall y \in Y$, $\mu(\omega)$ the chemical potential

For the equilibrium states of Σ the preasure function $\hat{p}: \mathbb{R}_+ \times \mathbb{R} \to \mathbb{R}$ is

$$\hat{p}(\theta,\mu) = -\inf_{\omega \in \xi(\Omega_T)} \hat{f}^{\phi}_{\theta}(\omega) = \inf_{\omega \in \Omega_T} \hat{f}^{\phi}_{\theta}(\omega)$$

where μ is related to ϕ through

$$\phi = \phi' - \mu\,\psi \qquad \text{with } \phi' \neq \phi'(\mu) \text{ and } \psi \text{ as in } (I.1)$$

(*) The $\wedge$ symbol above Σ is to signify it refers to this mean field system in particular.

The definitions of stability and equilibrium are just those stated before; adapted to the spatially ergodic states they read (VDW will stand for Van der Waals):

Definition VDW

i) $\hat{K}_L(\theta,\phi) = \{\omega \in \mathcal{E}(\Omega_T) \mid \omega \in K_L(\theta, \phi - \lambda\psi),\ \mathcal{J}\mu^{\psi}(\omega) = \lambda\}$

ii) $\hat{K}_G(\theta,\phi) = \{\omega \in \mathcal{E}(\Omega_T) \mid \hat{f}_\theta^{\phi}(\omega) = \inf_{\omega \in \mathcal{E}(\Omega_T)} \hat{f}_\theta^{\phi}(\omega)\}$

iii) $\hat{K}_E(\theta,\phi) = \hat{K}_G(\theta,\phi) \cap \hat{K}_L(\theta,\phi) \quad \omega \in \mathcal{E}(\Omega_T)$

iv) $\hat{K}_G^D(\theta,\phi)$ (the set of globally D-stable ergodic states of $\hat{\Sigma}$) $= \{\omega \in \mathcal{E}(\Omega_T) \mid \exists \eta > 0 \cdot \ni \cdot$ $\hat{f}_\theta^{\phi}(\omega') \geq \hat{f}_\theta^{\phi}(\omega) \quad \forall\, \omega' \in \mathcal{E}(\Omega_T)$, and $|\mu^{\psi}(\omega') - \mu^{\psi}(\omega)| < \eta\}$

v) $\hat{K}_M^D(\theta,\phi)$ (the set of D-metastable ergodic states of $\hat{\Sigma}$) $= \hat{K}_L(\theta,\phi) \cap \hat{K}_L^D(\theta,\phi) \setminus \hat{K}_G(\theta,\phi)$

A point to mention is that Def.VDW iv) defines a kind of stability related to infinitesimal alterations of the particle density $\mu^{\psi}(\omega)$.

Now it is possible to see to what extent can be said that Eq.L.Prop. i),ii) and iii) hold. It follows from its definition and the linearity of $\hat{f}_\theta^{\phi}$ in μ that $\hat{p}(\theta,\phi)$ is convex in μ and therefore generates the desired thermodynamics for the equilibrium state[19].

That the preasure for the metastable state is an analytic continuation in μ of that of the equilibrium phase is a result that follows after a lenghtly proof and since the details are not essential then only the conclusions will be quoted.

Let $q: \mathbb{R}_+ \times \mathbb{R} \times \mathbb{R} \to \mathbb{R}$ be given by

$$q(\theta, \mu | \lambda) = p(\theta, \lambda + \mu) - \lambda^2/2g$$

and let the sets $\Lambda(\theta, \mu)$, $\Lambda'(\theta, \mu)$ be defined by

$$\Lambda(\theta, \mu) = \{\lambda \in \mathbb{R} \mid q(\theta, \mu | \lambda) \text{ is absolutely maximal}\}$$

$$\Lambda'(\theta, \mu) = \{\lambda \in \mathbb{R} \mid q(\theta, \mu | \lambda) \text{ is strictly locally maximal}\}$$

then the following propositions follow:

Prop. VDW i) $\hat{k}_E^D(\theta, \phi) = \bigcup_{\lambda \in \Lambda(\theta, \mu)} \xi(K_G(\theta, \phi - \lambda\psi))$

ii) $\hat{k}_M^D(\theta, \phi) = \bigcup_{\lambda \in \Lambda'(\theta, \mu)} \xi(K_G(\theta, \phi - \lambda\psi))$

iii) If $\lambda \in \Lambda(\theta, \mu) \cap \Lambda'(\theta, \mu)$ and

$$\omega \in \xi(K_G(\theta, \phi - \lambda\psi)) \quad (\subset \hat{k}_E(\theta, \phi) \cap \hat{k}_M(\theta, \phi))$$

then

$$\lambda = g\mu^{\psi}(\omega) \quad \text{and} \quad \hat{f}_\theta^{\phi}(\omega) = -q(\theta, \mu | \lambda)$$

These results must be complemented with conditions expressing the existence and interrelation of the extreme values of the pressure. For this matter a map $\mu_c: J \to \mathbb{R}$ is defined (assuming the existence af such $\theta \in J$) with the property that for each $\theta \in J$ there is an open neighborhood $\mathcal{O}_\theta$ of $\mu_c(\theta)$ for whom the following propositions hold[20] (See the reference for the reason of this choice):

P.P. VDW i) There are precisely two values of λ denoted by $\lambda_1(\theta, \mu)$ and $\lambda_2(\theta, \mu)$ at which $q(\theta, \mu | \lambda)$ has maxima. In addition

$$q(\theta,\mu/\lambda_1(\theta,\mu)) \lesssim q(\theta,\mu/\lambda_2(\theta,\mu)) \quad \text{for } \mu \gtrless \mu_c(\theta)$$

ii) If $p(\theta,\mu')$ is real analytic in μ and and $g\left(\partial^2 p(\theta,\mu')/\partial\mu'^2\right) \neq 1$ for $\mu' = \mu + \lambda_i(\theta,\mu)$ $\mu \in \mathcal{D}_\theta$ then the functions $\mu(\in \mathcal{D}_\theta) \to q(\theta,\mu/\lambda_i(\theta,\mu))$ are real analytic for i=1,2.

Hence, by Prop. VDW i) and P.P. VDW i) it follows that

$$\xi\left(K_G(\theta,\phi-\lambda_1(\theta,\mu)\psi\right) = \begin{cases} \text{equilibrium states for } \mu < \mu_c(\theta) \\ \text{metastable states for } \mu > \mu_c(\theta) \end{cases}$$

if λ_2 is used instead of λ_1 the result still holds with "equilibrium" and "metastable" exchanging places. Then, by using Prop VDW iii) and P.P. VDW ii) the conclusion is made that the pressure $q(\theta,\mu/\lambda_2(\theta,\mu))$ for the metastable phase $(\mu < \mu_c(\theta))$ is a real analytic continuation in μ of that of the equilibrium phase $(\mu > \mu_c(\theta))$. The same can be said about $q(\theta,\mu/\lambda_1(\theta,\mu))$ if the inequalities between parentheses are reversed. Thus Eq.L.Prop. ii) is satisfied.

Trouble starts when inquiring about the lifetime of metastable states which in this case should be infinite or at least large enough. "Large" in this context is not precise since in general it will depend on the model being used, the way limits are taken and so on. The main problem is the absence of a kinetic theory general enough so as to give acceptable results regarding the stability of the states in question. If the type of kinetic theory used by Holley[21] (See Appendix A) -where a markovian master equation with detailed balance

was assumed is applied to the lattice systems studied by Sewell[2] then the local stability of the states implies the desired stability against environmental perturbations. In addition to this case there are other results concerning other forms of kinetics like the one used by Penrose and Lebowitz[30] supporting the existence of states with long enough lifetimes. Thus, as Sewell suggests, it seems reasonable to make the conjecture (for the time being) that locally stable states are dynamically stable against perturbations due to the interactions with the thermal reservoir, consequently providing equilibrium and metastable states with infinite lifetimes.

STABILITY IN THE QUANTUM LATTICE

Appart from the great gap in the dynamical aspects of the theory the very existence of models showing the desired features bring support to the characterization of metastability through the interplay of the so called global and local stability properties of the system.

That such formulation of metastability is in fact extendable beyond classical systems was proved by Sewell itself in a paper[22] where a quantum lattice system with the appropriate long range forces was seen to possess metastable states. The definitions used for the different kinds of states were just the generalization of those given before[3,22,23,24].

The main adaptation consisted in defining local thermodynamical stability for a state δ on $\mathcal{U}$ in terms of the

variational principle

$$\tilde{F}_{\Lambda}^{\beta}(\gamma) \leq \tilde{F}_{\Lambda}^{\beta}(\varphi) \qquad \forall\, \Lambda \in \mathcal{L} \equiv \{\text{the set of bounded regions of the lattice}\}$$

and $\forall\, \varphi \in \mathcal{U} \ni \varphi_{\Lambda^c} = \gamma_{\Lambda^c}$

β is the inverse temperature.

In here

$$\tilde{F}_{\Lambda}^{\beta}(\gamma) = \gamma(\tilde{H}_{\Lambda}) - \beta^{-1}\tilde{S}_{\Lambda}(\gamma)$$

$$\gamma(A) = \zeta_A(\rho_{\Lambda}^{\gamma} A) \qquad \forall\, A \in \mathcal{U}(\Lambda) \text{ and}$$

$$S_{\Lambda}(\gamma) = -\zeta_{\Lambda}(\rho_{\Lambda}^{\phi} \log \rho_{\Lambda}^{\phi}) \quad (*)$$

It was proved that LTS (local thermodynamical stability) in the case of quantum lattice systems[23,24] are equivalent to the KMS condition[1,4,7,25] hence supplying a further characterization for local stability. This is important since similar results had already been proved by Haag et al[26] in a quantum case, Lebowitz et al[27] for finite classical systems and by Aisenman et al[28] for infinite classical systems. The importance of this lying in that the KMS condition in many cases has been shown to imply the state inquestion is a Gibbs state (See Appendix $\mathcal{B}$). Up to now, in the case studied by Sewell the results only go as far as showing that LTS is equivalent to KMS for the quantum lattice system and LTS KMS DLR[5,27,28] for classical lattice and hard core continuous system.

(*) $\rho_{\Lambda}^{\gamma}(\in \mathcal{U}(\Lambda))$ is the density matrix corresponding tothe state γ on $\mathcal{U}$ and the region Λ.

ζ is the tracial state on $\mathcal{U}$.

And there is even more. In an article written by Kossakowsky et al[29] they presented a quantum system whose evolution was governed by a markovian master equation. This equation was assumed to satisfy a suitable defined balance condition. Under this condition they proved that for a certain "reduced dynamics" the detailed balance and the KMS condition were equivalent. This is important in relation to the lack of existence of results about the conjecture stating that local stability implies dynamical stability. Up to now in certain approaches to the metastability problem the detailed balance condition has been used as one of the conditions to obtain metastable states (even though to my knowledge it has not been proved to be an essential condition) . This rises the idea that it might be possible to relate LTS and dynamical stability by means of stablishing the connection

LTS $\longrightarrow$ KMS $\longrightarrow$ detailed balance condition $\longrightarrow$ existence of metastable states $\longrightarrow$ dynamical stability .

Section 11. ANALITIC CONTINUATION OF THE STABLE STATE.

The isotherms in the P vs f^{-1} graph[31] for the Van der Waals equation of state suggests a metastable state can be obtained as the analytic continuation of a stable equilibrium state thus explaining its equilibrium like properties. The non generality of such assumption was proved by Lanford and Ruelle[17]. They have shown that in the case of lattice gasses with finite range forces a metastable state obtained as mentioned above, can not exist.

Their reasoning goes as follows: given $\psi \in \underline{\Phi}$ and $a_\psi \in \mathcal{U}$ (the C*-algebra of observables) by definition an invariant state ω on $\mathcal{U}$ is an invariant equilibrium state for the interaction ψ if

$$P(\phi + \psi) = P(\phi) - \omega(a_\psi) \qquad \forall\, \psi \in \underline{\Phi}$$

where P is the pressure and given by

$$P(\phi) = \lim_{\alpha \to \infty} P_\alpha(\phi) = \lim_{\alpha \to \infty} \frac{1}{N(\alpha)} \log \sum_{x_\alpha \subset \alpha} \exp\left[-U_\phi(x_\alpha)\right]$$

and $$U_\phi(x_\alpha) = \sum_{x_\alpha \subset \alpha} \phi(x_\alpha)$$

In addition, if for finite $\alpha \subset \mathbb{Z}^\nu$ and $f_\alpha \in \zeta(x_\alpha) \times \mathcal{C}(\mathbb{Z}^\nu \setminus \alpha)$ the function f_α is defined as

$$f_\alpha(x_\alpha, y_\alpha) = \exp\left[-\sum_{s \subset x_\alpha \cap y_\alpha \,:\, s \cap x_\alpha \neq 0} \phi(s)\right]$$

then Lanford and Ruelle proved that

Theorem

An invariant state is an invariant equilibrium state if and only if for all α and χ_α

$$\omega_\alpha(\chi_\alpha, dy_\alpha) = f_\alpha(\chi_\alpha, y_\alpha)\,\omega_\alpha(\phi, dy_\alpha) \qquad (I.2)$$

where the state ω on $\mathcal{U}$ is the same as a probability measure on the set of configurations of the system and ω is related to f through the formula

$$\omega(f_\alpha) = \sum_{\chi_\alpha \subset \alpha} \int f_\alpha(\chi_\alpha \cup y_\alpha)\,\omega_\alpha(\chi_\alpha, dy_\alpha)$$

It is seen [17, Appendix A] that if ω satisfies equation (I.2) then

$$\lim_{\alpha \to \infty} \inf \frac{1}{N(\alpha)} \left[S(f_\alpha) - \omega_\alpha(U_\phi) \right] \geq P(\phi)$$

therefore discarding the existence of a metastable state characterized by

$$s(\omega) - \omega(a_\phi) < P(\phi) \qquad a \in \mathcal{U}$$

This is the first negative result concerning the existence of metastable states. The second negative result states that for finite range interactions the presence of a phase transition automatically excludes the existence of any state ω such that in a neighborhood of z_0 (*) the correlation functions $\xi(\chi_\alpha)$ are real analytic functions and ξ being the stable equilibrium state for $z \leq z_0$.

(*) $z = \exp(-2\beta H)$ is known as the activity

This result was in agreement with an earlier conjecture due to Fisher[32], namely that as an analytic function of z, P must exhibit a singularity at the point z_0 of a first order phase transition, result that was later proved by Dobrushin et al. But this does not mean that metastable states as analytic continuation of stable ones cannot be obtained; in fact the result concerns only those systems with short range interaction. To show that under different sorts of interactions the analytic continuation is valid has already been done while reviewing Sewell's work. Another example is the Felderhof - fisher model[3,33] and the models that will be seen in the remaining part of the section.

From what has been said before the appearence of singularities is an important element in the problem of metastability and therefore more attention was given to it by investigators.

While studying the properties of an Ising system near the condensation point, Langer[35] obtained interesting results. The problem was whether the Mayer cluster expansion (see Apendix C)[36,37] exhibited the first singularity at the condensation point $z = 1$ or at some $z > 1$, the so called " limit of metastability". Based on (39) it had been conjectured that there was no singularity at $z = 1$ hence the free energy could be analitically continued from the inside to the outside of the unitary circle. But at the same time the droplet model[40] of condensation implied that F (free energy) had an essential singularity at the con-...

densation point. In order to get a clearer view of this apparent paradox Langer analized the droplet picture of the Ising model[41,35] which postulates a free energy per particle of the equivalent lattice gas[42] of down spins as given by

$$f(H) = \frac{1}{N} \sum_{l=1}^{\infty} \nu_l(H) = \sum_{l=1}^{\infty} \exp\left[-\beta\left(2Hl + \sigma l^{(d-1)/d}\right)\right] \qquad (I.3)$$

where $\nu_l = N \exp(-\beta \phi_l)$ is the free energy of the cluster of l down spins and N the total number of lattice sites H is the magnetic field.

ϕ_l is assumed to be approximated by

$$\phi_l \simeq 2Hl + \sigma l^{(d-1)/d}$$

with $d \equiv$ dimensionality of the system, $\sigma \equiv$ surface tension of the droplet, and β will be assumed to be such that $\beta \geq \beta_c$ (β_c denotes the Curie point).

According to the Mayer series expansion[36]

$$f = \sum_{l=1}^{\infty} b_l z^l$$

where $z = e^{-2\beta H}$ and $b_l = \exp(-\beta \sigma l^{(d-1)/d})$. If l_c stands for the critical droplet (cluster) size, then the free energy of a metastable state, if it can be maintained (ie. there are no droplets being formed with $l > l_c$) is expected to be

$$\bar{f}(H) = \frac{1}{N} \sum_{l=1}^{l_c} V_l(H)$$

By differentiating ϕ_l we obtain l_c to be

$$l_c = \left[\frac{(d-1)\sigma}{2d|H|} \right]^d \qquad d \geq 2$$

The result of Langer's analysis with respect to the behaviour of $f(H)$ shows that at $H=0$ ($Z=1$), $f(H)$ diverges having a branch point singularity. The analytic continuation was obtained by approximating $f(H)$ by an integral and then moving H around the origin in the complex H-plane. Placing the branch cut along the negative H axis and keeping H very small the discontinuity in going from H_A to H_L (H_A in the upper half H-plane with $Re\, H_A < 0$ and H_L in the lower half H-plane with $Re\, H_L < 0$) was approximated by

$$f(H_A) - f(H_L) \simeq \frac{i\sigma}{\beta H^2}^{3/2} \exp\left[\frac{\beta \sigma^3}{27 H^2} \right] \qquad (I.3')$$

enabling f to be given as (for small H)

$$f(-|H| \pm i\,0) = \bar{f}(H) \pm \frac{1}{2} \left[f(H_A) - f(H_L) \right] \qquad (I.4)$$

where as said before $\bar{f}(H)$ is the free energy for the metastable state . From (I.3) it is seen that all its derivatives vanish at $H=0$; such is not the case for $f(H)$ whose derivatives of all orders are finite. Equation (I.4) tells the metastable phase free energy is just the real part of the analytic continuation of $f(H)$ for $Re\, H < 0$. The calculation of $\bar{f}$ can be done by cutting off the series (I.3) at $l = l_c$ and the error involved in doing so will be of the order of the

term containing λ_c. This happens to be a measure of the lack of definition, for this model, of the metastable phase. It implies there is no unique analytic continuation of the free energy into the metastable phase. Nevertheless, in respect to the presence of the essential singularity the consequences of its existence proved to be experimentally unobservable.

Section 111. EIGENVALUES AND METASTABILITY

Quantum mechanics has provided more than one approach to metastability, the most appealing feature being the one referring to the degeneracy of the eigenvalues corresponding to an operator with direct relevance to the system's behaviour.

This picture is somehow ambiguous because (as will be seen later) there is no unique operator which can be the subject of study hence the interpretation of the eigenvalues will differ according to the operator to which they cor-espond. On occasions the eigenvalues will just be the growth rate of the nucleation as in Langer's method for the first-principles calculation of the decay rate of a metastable phase[46]. More recent examples are Bak and Lebowitz[47] and Penrose and Lebowitz[30]. Generally speaking these authors were studying the nucleation rates and this problem inmediately determined what sort of objects the eigenvalues would be. But when the problem confronted is the analycity of the free energy then one of the possibilities is to relate or even reduce it to the properties of the partition function, in which case the eigenvalues under study will be those of the partition function. A different approach sees the decay process as an eigenvalue problem of multi-well potentials in quantum mechanics, the eigenvalues being those appearing in the solution of a Schroedinger-like equation into which a Fokker-Planck equation has been transformed[48].

All this ways of looking at metastability provide, if

not a complete solution, a better understanding of what the relevant parameters are if one wishes to construct a global theory of metastability. With this in mind it is worthwhile to take a closer look at the aims and achievements of these studies.

METHOD BASED ON THE DEGENERACY OF THE EIGENVALUES ASSOCIATED TO THE TRANSFER MATRIX

Since Yang and Lee[43,42] pointed out the significance of the zeros of the grand partition function a great deal of effort has been expended in finding its analytic consequences. A very fruitful method is using series expansions, with which expansion to use depending on the problem being tackled.

One way of attacking the problem is by exploiting an essential connection between the law of matrix multiplication and summations over all permissible configurations subject to a constraint. In the case of an Ising model such propertiy carries a great simplification to the calculation of the partition function[41]. Once written as a product of matrices, and with all the interactions being alike, the matrix product becomes a power and the sum over all configurations is the trace of the N^{th} power (where N is the number of spins) of the matrix. This special matrix is called "the transfer matrix and in the case of a two dimensional Ising model its relation to the partition function for an $m \times n$ lattice with periodic

boundary conditions is

$$Z_{m,n}(h) = Tr\{[L_n(h)]^m\}$$

where $L_n(h)$ is the transfer matrix, and $Z_{m,n}(h)$ the partition function. In terms of $Z_{m,n}(h)$ the infinite volume limit for the free energy is (for $h \in \mathbb{R}$)

$$\frac{f^{\circ}(h)}{kT} = -\lim_{m,n\to\infty} (1/mn) \log Z_{m,n}(h) = -\lim_{m,\to\infty} (1/n) \log \lambda_n^{\circ}(h)$$

where $\lambda_n^{\circ}(h) > \lambda_n'(h) \geq \lambda_n^{2}(h) \geq \dots \geq \lambda_n^{2^n} \geq 0$

are the eigenvalues of $L_n(h)$.

It will be conceptually and physically interesting to obtain metastability without recurring to the thermodynamic limit hence the importance of the attempt carried out along these lines by Newman and Schulman[44] (NS from now on).

NS considered particular functions whose thermodynamic limit coincides with that of the usual thermodynamic functions and in addition possess a multivalued branch for the finite system. These functions described models whose free energy in the thermodynamic limit is related to the minimum eigen - value of the transfer matrix. The occurrence of a phase transition is associated with the asymtotic degeneracy of the eigenvalue. What NS wanted was to obtain, for a finite system, the metastable states as analytic continuation of the equilibrium states. To this effect they allowed particulat thermodynamic variables to take complex values and the desired analytic continuation was carried out from the region where a par-

ticular eigenvalue was the minimum eigenvalue to a region where this is no longer so.

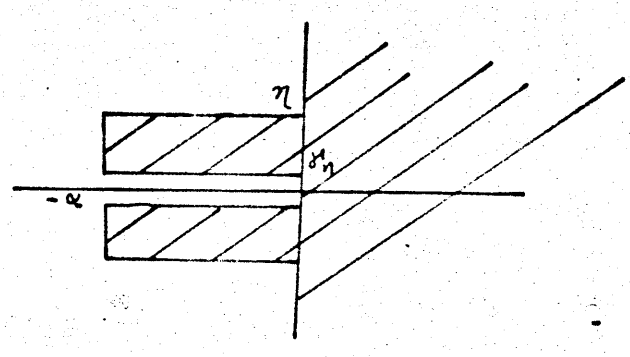
Addapting these ideas to the Ising model presented above $E_n^{\vec{s}}(h)$ was defined as

$$E_{\vec{s}}^{n}(h) = -(1/n)\log \lambda_n^{\vec{s}}(h)$$

According to NS[44] $E_n^{\circ}(h)$ and $f^{\circ}(h)$ are analytic on both tight and left half plane of complex h, and the magnetization m has the same sign as h. While continuing E_n° from the region where $h>0$ to the region where $h<0$ (for $T<T_c \equiv$ critical temperature) it was seen that in order to keep the same sign for $m(h)$ a path avoiding the origin has to be taken.

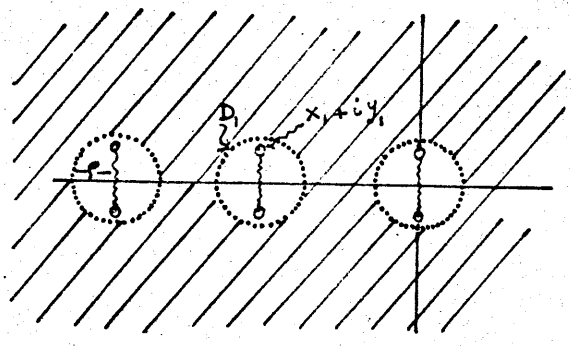
From a study made on simpler models it was then conjectured

1° That for $T<T_c$ there were regions D_n (excluding the point $h=0$) of the complex h-plane where E_n° could be analytically continued to a function $E_n^{+}(h)$ analytic single valued and uniformly convergent to $f^{+}(h)$ which also was analytic on D_n and such that for $Re\ h > 0$ $f^{+}(h) = f^{\circ}(h)$



2° That near the negative real axis there were points $\chi_k(n)$ ($k=1,2,\dots$) with the property that $E_n^+(h)$ was analytic on $\mathcal{D}_n$ except on neighborhoods $V(\chi_k)$ containing the χ_k's (with size of $V(\chi_{k(n)})$ shrinking to zero as $n\to\infty$).

3° That the $E_n^+(h)$ could still be continued into these neighborhoods with the solely exception of two branch points (for each k) connected by a square root branch cut.



NS claim that the analytic continuation $E_n^+(h)$ carried around the branch cut is the one responsible for the metastable state.

With respect to the location of the first singularity of $f^+(h)$ this is placed on the negative realaxis and corresponds to the asymptotic merging $E_n^+(h)$ and the energy of the first excited metastable state. It also implies that the singularity has an infinite correlation length in the metastable state and, if taken as a function of T it then defines the spinodal line $h_s(T)$ (30) (the line separating the metastable from the unstable regions) ($h_s(T)\to 0$ as $T\to T_c$).

Taking the NS article as point of departure McCraw and Schulman[50] studied the behaviour of the transfer matrix eigenvalues, their connection to metastability and the support that can be given to such approach by way of comparing results with a dynamical Monte Carlo model.

Given a $N \times N$ lattice with periodic boundary conditions a small magnetic field was chosen so that the equilibrium magnetization m was close to -1, and the metastable value for m was chosen to be close to $+1$. Firstly NS assumed the decay rate Γ could be expressed as

$$\Gamma \sim \text{volume}\ e^{-\phi/T} \quad \text{with} \quad \phi(T,H) = T \log A$$

where H is the magnetic field and A the number of spin flips before decay. In here A will depend en H.

By performing the numerical calculations they showed $\phi(T,H)$ could be interpreted to be the free energy of a critical droplet, ie. the amount ΔE of energy needed in order to cross the energy barrier separating the metastable (relative minimum) from the stable state (absolute minimum). Monte Carlo data for $\phi(T,H)$ was used to obtain the graph of $\phi(T,H)$ vs. H In the case of ΔE the energy E was given by $E = -J\Sigma\sigma\sigma - H\Sigma\sigma$ with $J = 1$. The agreement in the values obtained for ϕ was the basis for the interpretation already mentioned.

Having made the connection between ϕ and its relation to the critical droplet an analytic expresion for ϕ was obtained, this being $\phi = 8J^2/|H|$ which in turn implies the decay

rate $\mathcal{P}$ is given by

$$\mathcal{P} = N^2 e^{-\beta J^2/|H|T}$$

where α is defined as $\alpha = -\beta J^2/|H|T$.

An interesting point in the NS article was the crossing of the transfer matrix eigenvalues and the appearance of a gap in the crossing, the gap bein related to the coupling of states. This is in fact corroborated by the numerical results of McCraw and Schulman (McCS from now on) showing that the value of H at which the crossing takes place was $|H| = 2J/\ell$. This is actually a good result since in the transfer matrix approach at this value of $|H|$, ℓ down spins can be interchanged for ℓ up-spins with no change in the energy and is also the Monte Carlo value of H needed for the appearance of the $\ell \times \ell$ critical droplet.

If in addition the 2-level model introduced by NS[44] is used, a further connection is obtained[50]. In this model the free energy shift ΔF was written by NS as

$$\Delta F \simeq 4\pi^2 \alpha^2 / N(H - H_c)\Delta m$$

where Δm is the increment in the magnetization value between the two levels and H is the crossing field. Comparing this formula with the Monte Carlo decay rate brings out that both quantities are proportional to α^2 hence relating the non concavity of F to the decay results.

Regarding the presence of a singularity in the complex

h-plane the question is answered in the positive; it was found that close to the negative real h-axis an infinity of singularities will appear, $h=0$ in particular being an essential one.

As already pointed out by NS a study of the Ising model without dynamics is like neglecting the quantized electromagnetic field when obtaining the energy from the coulomb force for one of the energy levels of the hydrogen atom. Thus it is expected that metastable features will hardly be shown. Nevertheless, when the phase transition is related to eigenvalue degeneracy it seems the analysis of the transfer matrix's eigenvalues is a "first approximation" qualitative picture of how a metastable state in a model with dynamics would behave. From the work of McCS it is seen that such is the case for the model they studied.

Transformation of a Fokker-Planck equation to a Schroedinger-like equation whose eigenvalues represent the decay rate.

The idea of relating eigenvalues to stability aspects provided another approach to the study of metastable states. Starting from a Fokker-Planck equation Tomita et al[48] (TIC from now on) exploited the formal analogies assumed to exist between stochastic processes and quantum mechanics. This work comes as a possible alternative to the system-size expansion (Ω-expansion) developped by Kubo et al[51] with the purpose of dealing with far from equilibrium situations. Under this condition, according to Tomita, local stability cannot account for the relaxation to equilibrium and any information about de-

cay rates has to come from the global stability of the system.

The method of TIC consisted in transforming the markovian master equation

$$\frac{\partial}{\partial t} P(x,t) = -\mathcal{L}[x]\, P(x,t)$$

where $\mathcal{L}[x]$ is the markovian evolution operator, x the stochastic variable and $P(x,t)$ the probability distribution function, into

$$-\varepsilon \frac{\partial}{\partial t} \psi(x,t) = \mathcal{H}[x]\, \psi(x,t) \qquad (I.5)$$

where the relation between ψ and P is $P(x,t) = P_o^{1/2}(x)\, \psi(x,t)$ $\mathcal{H}[x]$ is self-adjoint and hermitean and ε is a size parameter. ($\mathcal{H}[x] \equiv -\varepsilon^2 \frac{\partial^2}{\partial x^2} + V(x)$ and $V(x) \equiv \left(\frac{F'(x)}{2}\right)^2 - \frac{\varepsilon}{2} F''(x)$ $F(x) \equiv -\varepsilon \log P_o(x)$

A simple example can be given to clarify what the symbols stand for. Let $P(x,t)$ be a time dependent probability distribution, of which a wave function would be a particular case. A Fokker-Planck example is

$$\frac{\partial}{\partial t} P(x,t) = \left[-\frac{\partial}{\partial x} c_1(x) + \frac{\varepsilon}{2} \frac{\partial^2}{\partial x^2} c_2(x)\right] P(x,t) \qquad (I.6)$$

By direct calculation it can be shown that by defining

$$V(x) = \frac{1}{2c_2(x)} \left[c_1(x) - \frac{\varepsilon}{2} c_2'(x)\right]^2 + \frac{\varepsilon}{2} \left[c_1(x) - \frac{\varepsilon}{2} c_2'(x)\right]'$$

$$P_0(x) \propto \exp\left\{ \frac{2}{\varepsilon} \int^x \frac{c_1(x) - \varepsilon/2\, c_2'(s)}{c_2(s)}\, ds \right\}$$

and $\Psi(x,t)$ as in I.5 , equation (I.6) is transformed into

$$-\frac{\varepsilon}{\partial t}\Psi(x,t) = \left[-\frac{\varepsilon^2}{2}\frac{\partial}{\partial x} c_2(x) \frac{\partial}{\partial x} + V(x)\right] \Psi(s,t) \quad (I.7)$$

Here ε is a size parameter corresponding to Planck's constant h . Appart from $\frac{1}{c_2(x)}$ being a space-dependent mass, equation (I.7) is a Schroedinger equation for one particle in a one dimensional potential, thus showing how the transformation can be made from the original master equetion and at the same time provide an example of what sort of object the markovian evolution operator is.

The only assumptions leading to (I.5) (appart from having taken a simple Fokker-Planck equation to be transformed, but this detail is not essential for the discussion) were the existence of an equilibrium distribution $P_0(x)$ for which a detailed balance condition is satisfied.The connection to thermodynamics was made through the equality

$$F(x) = -\varepsilon \log P_0(x)$$

where $F(x)$ was identified with the free energy.

Once again the method is better illustrated by taking a particular model. The model chosen is one whose interaction potential $V(x)$ gave a free energy of the form

$$F(x) = \frac{1}{2}\left\{(1+x)\log(1+x) + (1-x)\log(1-x) - \frac{\beta}{2}x^2 - \beta H x\right\}$$

where $\beta = \frac{1}{KT}$

This function, when represented in a graph, looks like Fig. 1

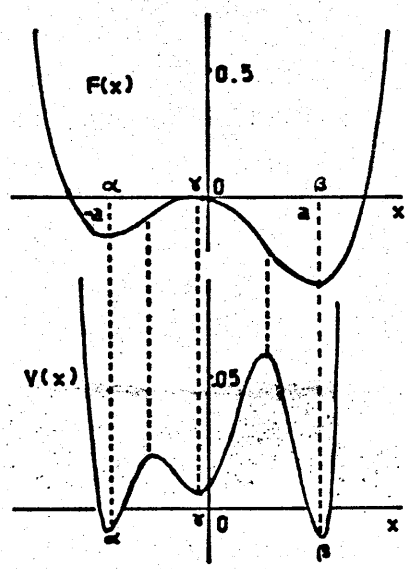


Fig. 1

If we assume the initial metastable state is the left half part of the equilibrium distribution this means that at $t = 0$

i) $P(x,0) = P_0(x)\,\theta(\gamma - x)/W(\infty)$ $\qquad \theta(y) = \begin{cases} 1 & y \geq 0 \\ 0 & y < 0 \end{cases}$

ii) $\psi(x,0) = \phi_0(x)\,\theta(\gamma - x)/W(\infty)$

iii) $W(\infty) = \int_{-\infty}^{\gamma} P_0(x)\,dx$

A measure of the decay process was defined as

$$W(t) = \int_{-\infty}^{\gamma} P(x,t)\,dx = W(\infty)\left\{1 + \sum_{n=1}^{\infty} a_n^2 \exp(-\lambda_n t)\right\}$$

which relaxes to unity. The λ_n's come from the sol tion of the eigenvalue problem for (I.5) .

For a high enough value of F at γ the decay constants, ie. energy levels $\{\lambda_n\}$, are expected to be such that

$$\lambda_2 \gg \lambda_1 \approx \lambda_0 \ (\approx 0)$$

so that when $\lambda_0 = 0$, λ_1 will stand for the decay rate of the metastable state. Then the last part of the decay process can be approximated by (see Fig. 2)

$$\psi(x,t) \cong \phi_0 + a_1 \phi_1 e^{-\lambda_1 t} \simeq \phi_0 + a_1 \phi_1$$

$$P(x,t) \cong P_0(x) + a_1 \phi_0 \phi_1 e^{-\lambda_1 t} \simeq P_0(x) + a_1 \phi_0 \phi_1$$

$$W(t) \cong W(\infty)\{1 + a_1^2 e^{-\lambda_1 t}\} \cong W(\infty)\{1 + a_1^2\}$$

where λ_0 , λ_1 were the eigenvalues for the ground and first excited states and therefore the original wave function can be constructed as $\phi_0 + \phi_1$ with

$$\phi_0(x) \simeq (\psi_L(x) + \psi_R(x))/\sqrt{2}$$

$$\phi_1(x) \simeq (\psi_L(x) - \psi_R(x))/\sqrt{2}$$

and $\psi_R(x)$ and $\psi_L(x)$ were the ground states in the right and left hand wells of the potential respectively.

The change in time of the distribution function $P(x,t)$ ie. the decay rate, will be like in Fig. 2 where the change of the wave function $\psi(x,t) - \phi_0(x) \simeq a_1 \exp(-\lambda_1 t)\, \phi_1(x)$ is also plotted

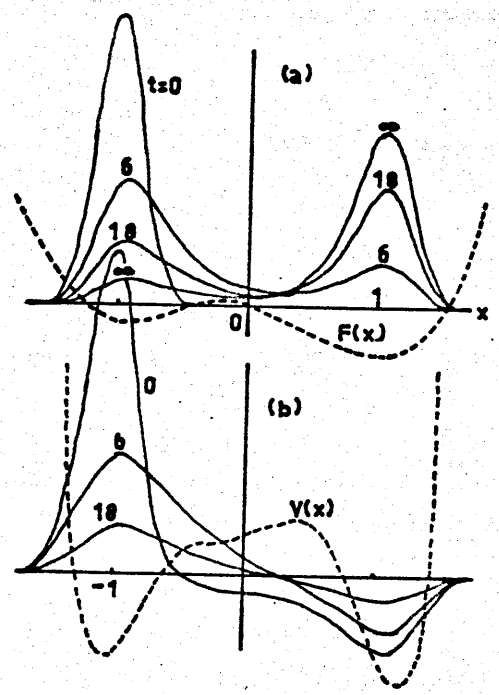


Fig. 2

The existence of two time scales is clearly discernable thus unabling us to interpret the relaxation to equilibrium as a two-step process (even though a sharp definition between the two scales cannot be given) :

1° Relaxation to a metastable distribution.

2° (In a time considerably smaller than in 1°) Penetration through the energy barrier of the probability distribution.

Qualitatively this offers a nice picture of the decay process of a metastable phase. Unfortunely the kind of Fokker-Planck equation used is too simple and only covers problems describable in terms of one variable hence making it useless in cases closer to what a real physical system is. Another

point subject to criticism is that this method looses rigour when the initial state is an unstable one[48]. By means of another approach Shimizu[52] has studied both cases, his results having only formal importance since no calculations have been made using his treatement of the problem.

CHAPTER II. DYNAMIC ASPECTS OF METASTABILITY

Introduction. PENROSE AND LEBOWITZ ON METASTABILITY.

This method of characterizing metastable states [30] makes use of the direct physical description that can be given for these states. The phenomenology is translated into precise mathematical statements and then we proceed to show the existence of physical systems, or at least of mathematical models, showing the presence, under suitable conditions, of metastable states as defined in this section

Three general properties can be stated as characterizing the metastable thermodynamic states:

MP I) There is only one thermodynamic phase present but the values taken by the intensive parameters correspond to either:

i) an equilibrium state having more than one thermodynamic phase present, or

ii) an equilibrium state with a single phase but this phase not being the expected one.

MP II) While the system remains in isolation the rate of decay of the metastable state is very slow. Large enough and in consequence very improbable fluctuations provide the first stage of the mechanism through which the system is lead out of the metastable state.

MPIII) Once the system has gone out of the metastable state it is highly unlikely for it to return to

this state, or in other words, the process of leaving the metastable state is an irreversible one.

Metastable phenomena show both equilibrium and non-equilibrium type of behaviour therefore their description involves the two complementary conceptual apparatus of equilibrium and non-equilibrium statistical mechanics. The former is used to describe those features associated with the thermodynamics (or static properties) while the later is concerned with the irreversible processes ("dynamic" properties) driving the decay of the metastable state.

The static properties (described in MP I) will be given by the already developed formalism of statistical mechanics applied to a suitably defined ensemble.

Underlying the characterization of metastability given above is the consideration of the existence of two types of mechanisms affecting the system. There is a fast one that sets the metastable state up and a slow one being the cause of the properties we ask a mhtastable state to satisfy[48,53]. The Penrose and Lebowitz (PL from now on) treatement of metastability assumes the first mechanism to have already acted and the description concerns, generally speaking, only the effects of the slow processes occurring within the system.

When dealing with this method the first problem is to choose the appropriate region Γ_M in configuration space

where the metastable state belongs. This is done by using criteria MP 1,11 and 111, ie. a restriction is imposed on the system, keeping because of this a roughly uniform density.This will be mirrored on configuration space by the motion of the representative point being confined to a certain region Γ_M of phase space. This can be done formally by defining a modified system differing from the original by an extra term that is added to the hamiltonian, the term having the value 0 for configurations in Γ_M and the value $+\infty$ for configurations outside Γ_M .

The equilibrium-like behaviour of the metastable state suggests the possibility of using the formalism of stable equilibrium statistical mechanics for the description of the stati properties. Such properties of the points in Γ_M can therefore be found by applying the Gibbs ensemble method to the region Γ_M so that the probability distribution for the points $\xi \in \Gamma$ will be

$$P(\xi) = \begin{cases} \text{const. } e^{-H(\xi)\beta} & \text{if } \xi \in \Gamma_M \\ 0 & \text{otherwise} \end{cases}$$

Such an ensemble is called the "restricted equilibrium ensemble".

To ensure that the region Γ_M so defined satisfies MP11 we consider the dynamical aspects of the problem. This is done by studying the evolution in time of the restricted ensemble under the action of the original hamiltonian. In such terms

the probability $p_\xi(t)$ for the point ξ to have gone out of Γ_M will be equal to the fraction of members of Γ_M that are no longer in Γ_M at time t. Once all transients have died out the rate

$$\lambda(t) = \frac{dp}{dt}(t)$$

will be the rate with which the metastable region is being abandoned by systems originally in Γ_M. It was proved by PL[10] that

$$\lambda(t) \leq \lambda(0)$$

hence if $\lambda(0)$ is sufficiently small then MP 11 will be satisfied.

In order for the system to satisfy MP 111 it is necessary that the region Γ_M should be formed by points representing a set of configurations highly improbable in the true equilibrium ensemble. The reason for this is a consequence of the restricted ensemble free energy density being always greater than that of the unrestricted ensemble. How great depending on a factor that is proportional to the size of the system and therefore the probability for ξ to be in Γ_M decreases exponentially as the system increases in size.

One of the first useful results of applying this method is the possibility of deriving the (metastable free energy) VS (density) graph in the Van der Waals-Maxwell theory of the vapor-liquid transition.

In the usual methods for obtaining the free energy density from the partition function, the result is that the free energy is always a convex function of the density ρ. But this result does not account for the phenomena of metastability and therefore an extension of the usual formalism of the Gibbs ensemble was necessary, so that points not on the convex envelope of the free energy density curve can be allowed as possible states of the system, these points representing the metastable states.

Up to now everything has been described in very general terms and without giving details of the rigorous mathematical definitions and calculations that must be carried out; to go more into detail ask for an specific physical system or mathematical model.

THE VAPOR-LIQUID TRANSITION.

PL have mainly studied the vapor-liquid transition for a system with very long range attractive interactions: the Van der Waals system[4,5,9,10].

This is a classical system of iden-ical particles each with mass m, and an interaction potential $v(\vec{r})$, given by

$$v(\vec{r}) = q(r) + \gamma^{\nu} \phi(\gamma r) \quad , \quad 0 \leq r < \infty$$

where $q(\vec{r})$ is the short range repulsive contribution to

the potential, $\gamma^{\nu}\phi(\gamma\bar{r})$ the weak long range attractive contribution, ν the number of dimensions and γ a parameter such that γ^{-1} is the range of the attractive potential.

Having in mind that the system was studied in the limit $\gamma \to 0$ the PL description goes as follows

i) The volume Ω occupied by the system is partitioned into imaginary cells $w_1, \ldots, w_n$ of equal size and the region Γ_M is defined as the set of points in the configuration space for which the number of particles (or density) in each one of the cells remains within a certain range of values If η_i is the number of particles in cell w_i then η_i satisfies $\eta_- \leq \eta_i \leq \eta_+$ with η_- and $\eta_+ \in \mathbb{R}^+$

ii) Having done this, now it has to be shown that the initial escape rate $\lambda(0)$ is small enough . PL proved $\lambda(0)$ can be expressed as $A B = \lambda(0)$ where

$A \equiv$ probability that the number of particles in some cell "i" is at the edge of the allowed range, ie. $\eta_i = \eta_-$ or $\eta_i = \eta_+$ for some "i".

$B \equiv$ the conditional probability that another particle will move into that cell.

and that upper bounds of A and B can be found having the form

$$A \leq \exp\{-c|\omega| + o|\omega|\}$$

where $|w| \equiv$ volume of cell w and $o|w|$ means a quantity which after division by $|w|$ tends to 0 as $|w|$ increases.

$$\mathcal{B} \leq \text{const.}\ |\Omega|\,|\omega|^{-1/\nu}$$

so that as a whole $\lambda(o)$ has an upper bound given by

$$\lambda_{(o)} \leq \text{const.}\ |\Omega|\,|\omega|^{-1/\nu} \exp\{-c|\omega| + o|\omega|\}$$

The constant c will be positive if $f_o''(\rho) + \alpha > 0$ (which is equivalent to asking for the compressibility to be positive) where f_o is the free energy density for the short range part of the potential and

$$\alpha \equiv \gamma^\nu \int_\Omega \phi(\gamma r)\, d^\nu \underline{r}$$

Under this conditions and provided that the thermodynamic limit is taken in such a way that

$$|\Omega| \gg \gamma^{-\nu} \gg |\omega| \gg \ln|\Omega|$$

the symbol $a \gg b$ meaning $\frac{a}{b} \to \infty$ then the escape rate can be made as small as desired and hence MPII is satisfied.

iii) As mentioned before, Γ_M has to be chosen so that the free energy density of the restricted ensemble

which can be shown to be

$$f_0(\rho) + \frac{1}{2}\alpha\rho^2$$

exceeds the free energy density of the true equilibrium ensemble, ie.

$$f(\rho, 0^+) \equiv \lim_{\gamma \to 0^+} f(\rho,\gamma) = CE\left[f_0(\rho) + \frac{1}{2}\alpha\rho^2\right] \leq f_0(\rho) + \frac{1}{2}\alpha\rho^2$$

where CE stands for convex envelope. This condition makes the relative weight of the region Γ_M very small and hence it will be highly improbable for such region Γ_M to be reached from outside. Given this condition it is seen that the third criteria MP III of metastability is also satisfied.

A remark has to be made and it is that the characterization of metastable states given by PL has demanded two essential and physically meaninful conditions:

$$f_0(\rho) + \frac{1}{2}\alpha\rho^2 > CE\left\{f_0(\rho) + \frac{1}{2}\alpha\rho^2\right\}$$

$$f_0''(\rho) + \alpha > 0$$

these being precissely Maxwell's conditions for metastability as obteined from the possibility of reaching all the points in the (free energy density VS density) graph with the excep-

tion of those points for which the system would be mechanically unstable. ie. for $\xi \in \Gamma$ such that

$$f_o''(f) + \alpha < o$$

KINETICS IN THE LATTICE GAS.

Since metastable states arise from a particular kind of behaviour outside equilibrium it is up to the kinetics of the system to give an insight on how the state is maintained, how nucleation is prevented and how it eventually may produce the appearance of the new phase. A non-rigorous but empirical approach was initiated by Becker and Döring[53] which considered the growth of individual droplets and applied the methods of chemical kinetics to estimate their growth. This approach was further explored by Frenkel[55,70,71,72] and his treatement forms the basis of modern nucleation theory[73]. Each droplet is treated as a sphere whose free energy depends on its surface and volume and is therefore determined by its radius. Some assumptions than in nucleation theory are reasonable were made namely that there are no interactions between droplets and that the possibility of different sizes and shapes of droplets are of secondary importance. This approach had an advantage over the cluster integral approach of Mayer[75], the advantage consisting in being mathematically simpler than Mayer's theory with its "mathematical intricacy (which) will hardly appeal to the experimental physicist or chemist". Since then theories on nucleation have been applied in the vapor-liquid transition and is largely responsible for what is now known concerning

the formation of droplets. Therefore it is desirable to make a connection between the concepts used in nucleation theory and the concepts of statistical mechanics used so far. This was carried out by PL[30] by first defining, in the lattice gas version of the Ising model[76] what a cluster of a given size would be. By assuming certain simplifications (to be made explicit later on) with respect to the processes considered, kinetics was introduced through the Becker-Döring set of equations[53] which describe how the size of the cluster changes due to absortion and evaporation of particles. The term cluster in this case will be equivalent to a droplet.

In terms of the grand canonical formalismthe static properties of the lattice gas can be obtained (in the equilibrium or the restricted ensemble). A sketch of the procedure goes as follows: let

$$\Xi(\Lambda, z, \beta) = \sum_{\xi} z^{N(\xi)} \exp(-\beta H(\xi)) \qquad (II.1)$$

where the sum goes over all configurations ξ of empty and non-empty sites on the given lattice, $N(\xi)$ is the number of occupied sites and $U(\xi) = H(\xi)$ is the energy of the configuration represented by ξ. The usual meaning is assigned to β and z ie. the inverse temperature and the activity respectively.

"Clusters" are defined to be maximal connected subsets of occupied sites into which the configuration ξ can be partitioned. That a set is connected means that no one member

of the set is a nearest neighbor of a member of another set but for every subdivision of a connected set into two subsets then at least one member of one subset is a nearest neighbor of a member of the other subset.

Once + or - boundary co-ditions are imposed, equation (II.1) can be written in terms of clusters as

$$\Xi = 1 + \sum_{\{c\}} \prod_i z^{N(c_i)} e^{-\beta U(c_i)} \qquad (II.2)$$

where $N(c_i)$ is the number of particles in the i-th cluster and $U(c_i)$ the corresponding potential energy. The sum is over the possible arrangements of the clusters $c_1, c_2, \ldots, c_i, \ldots$. At low densities and by extending the sum in equation (II.2) over all the impossible arrangements of clusters, ie. allowing clusters to overlap, it is shown that

$$\log \Xi \leq \sum_{N=1}^{|\Lambda|} z^N Z_N(\Lambda) \qquad (II.3)$$

where $|\Lambda|$ is the size of the lattice and

$$Z_N(\Lambda) = \sum_{c\,:\,N(c)=N} e^{-\beta U(c)}$$

with the sum in (II.3) going over all clusters with N sites.

If Q_N is defined as

$$Q_N \equiv \lim_{\text{large } \Lambda} (1/|\Lambda|) \sum_{c\,:\,N(c)=N} e^{-\beta U(c)} \qquad (II.4)$$

then Q_N can be thought as the internal partition function for clusters of size N .

After proving that

$$Z_N(\Lambda) \leq |\Lambda| \, Q_N$$

is true for any rectangular lattice it was shown that for z small enough for the series

$$\sum_{N=1}^{\infty} z^N Q_N$$

to converge, this series will provide an upper bound on

$$(1/|\Lambda|) \log \Xi$$

Along the same lines it is found that the probability $Q(c)$ that the cluster c is present in the system has an upper bound given by(*)

$$Q(c) \leq z^{N(c)} e^{-\beta U(c)} \qquad (II.5)$$

and therefore with m_N standing for the expected number of N-particle clusters per unit volume, ie. per lattice site

$$m_N = (1/|\Lambda|) \sum_{c : N(c)=N} Q(c) \leq (1/|\Lambda|) z^N Z_N(\Lambda) \leq z^N Q_N \qquad (II.6)$$

(*) Better upper bounds have been provided by Penrose and Lebowitz in a more recent paper(77).

Now an important step forward is given by introducing an internal free energy F_N defined as

$$F_N \equiv -(1/\beta) \log Q_N \qquad (II.7)$$

so that

$$m_N \leq Z^N e^{-\beta F_N} \qquad (II.8)$$

Once a lower bound to m_N is found the above inequality can provide a rigorous version of the Boltzmann-factor approximation $e^{-\beta \Delta F_N}$ to m_N used in nucleation theory.

In relation to metastability theory, the three properties MP I, II, III characterizing a metastable state are stated in terms of clusters by first defining what the restricted ensemble should be (among several possible ways of doing it).

The restricted ensemble was defined as the set of points in Γ representing configurations such that all clusters associated with these configurations have at most some specified number μ of sites.

Having done this the next step is to estimate the rate of escape from the ensemble, where escape means the formation of any cluster consisting of more than μ particles.

The movements of the particles are asumed to be governed by the Kawasaki dynamics[67,78]. Accordingly, a particle can only change position by going to a nearest neighbor site

if empty. The changes in the configuration are given at random with probability $\varphi(\Delta U)\exp(-\frac{1}{2}\Delta U/kT)$ where $\Delta U = U_f - U_i$ is the difference in energy between the new and the original configurations. The function $\varphi(\Delta U)$ is an even function of ΔU.

If the assumption of dealing with transition probabilities satisfying the principle of detailed balancing is made, a great simplification can be carried out and instead of summing the probabilities of all the possible combinations of processes bringing together clusters which will merge into a cluster larger than an μ-particle cluster, you can calculate the probabilities of $(\mu+i)$-particle clusters breaking up, with $i=1,\ldots,(q-2)+1=\theta$ where θ is the largest cluster that can be produced in a single step starting from a cluster compatible with the restricted ensemble.

Adding these probabilities gives an upper bound to the escape rate which if denoted as before by λ reads

$$\frac{\lambda}{|\Lambda|} \leq W_M\, q \sum_{n=\mu+1}^{(q-1)\mu+1} n\, Z^N Q_N \qquad (\text{II}.9)$$

With W_M being an upper bound on the probability per unit time that a given particle will move to a given empty neighboring site, q is the coordination number of the lattice, and Z and Q_N have already been defined before. Since (II.9) can be written as

$$\frac{\lambda}{|\Lambda|} \leq W_M\, q \sum_{n=\mu+1}^{(q-1)\mu+1} n \exp(-\Delta F_N/kT) \qquad (\text{II}.10)$$

it is seen how the escape rate can be made small by keeping

μ and $\exp(-\Delta F_N/kT)$ small enough and therefore showing that the rigorous theory of metastability is in agreement with the predictions of nucleation theory once the appropriate definitions have been made .

Turning now to the actual value of the rate of nucleation, this was expected to be bounded above by the escape rate due to, among other things, the fact that in the former the processes building large clusters from small ones are partially compensated by the inverse processes (ie. evaporation of a particle from an $(\mu+1)$-particle cluster), whereas in the escape rate processes a one way traffic was assumed.

The problem of the rate of nucleation was treated in terms of the Becker-Döring kinetics and under the assumption of dealing with a system at a very low density in which clusters are statistically independent. In processes involving the merging of clusters, only one of them was allowed to contain more than one particle.

Under the hypothesis of having a particle conserving dynamics this last assumption implies that the only way a particle cluster can grow is by absorbing a 1-particle cluster and conversely, the breaking of a (n+1)-particle cluster can only be done by emiting a 1-partcle cluster.

With these considerations the net rate of change of the number of η-particle clusters was written as[53]

$$\frac{d}{dt} m_n = J_{n-1} - J_n \qquad (II.11)$$

with

$$J_n = a_n m_n m_1 - b_{n+1} m_{n+1} \qquad (II.12)$$

where a_n, b_{n+1} are constants independent of time and

$$\frac{d}{dt} m_1 = \begin{cases} 0 \\ -\sum_{n=2}^{\infty} n(J_{n-1} - J_n) = -2J_1 - \sum_{n=2}^{\infty} J_n \end{cases} \qquad (II.13)$$

depending on whether m_1 is considered as not changing significantly with time or $\sum_{n=1}^{\infty} n m_n$ is the quantity that does not change in time. This last assumption is more realistic (in the case of Kawasaki dynamics) in taking the expectation of the total number of particles in the system as the quantity not changing in time.

Becker and Döring used the assumption that each time the size of a cluster passes a certain large value μ, the cluster is removed from the system which amounts to say

$$m_n = 0 \quad \text{if} \quad n > \mu \qquad (II.14)$$

and by choosing m_1 to be a constant, they found a steady state solution for $\frac{d}{dt} m_n$ $(n \geq 2)$ with J_n independent of n. This independency of J_n with respect to n is also consistent with the equation for $\frac{d}{dt} m_1$ when m_1 is a constant. Under these conditions the following result is found to hold:

$$\sum_{n=1}^{\mu} J_n R_n = m_1 \qquad (II.15)$$

where $R_n = \left((m_1)^n c_n a_n \right)^{-1} = (1/m_1^n) b_2 \ldots b_n / a_1 \ldots a_n \quad (n \geq 1)$

and the common value of $J_1, J_2, \ldots$ or in other words, the nucleation rate J is therefore given by

$$J = m_1 / \sum_{n=1}^{\mu} R_n \qquad (II.16)$$

thus expressing the nucleation rate in terms of microscopic quantities.

Comparison between the nucleation and the escape rate was done by altering the dynamics of the system so that this time no μ-particle cluster was allowed to increase in size. This was done in order to work with the restricted ensemble which in this case will be formed by those points representing configurations where no clusters having more than μ particles are allowed. Mathematically this means:

$$J_n = 0 \qquad (n \geq \mu) \qquad (II.17)$$

hence the equilibrium solutions to the kinetic equations come out to be

$$m_n = \begin{cases} C_n \, (m_1)^n & n \leq \mu \\ 0 & n > \mu \end{cases} \qquad (II.18)$$

With the above distribution at $t=0$ and no restrictions imposed on the kinetic equation (II.12), $\frac{d}{dt} m_{\mu+1}$, the probability per unit time, per unit volume of a cluster of

size $\mu+1$ to appear is

$$\left(\frac{d}{dt} m_{\mu+1}\right)_{t=0^+} = J - J_{\mu+1} = J_\mu = a_\mu c_n (m_1)^{+1} \qquad (II.19)$$

$$\left(\frac{d}{dt} m_{\mu+1}\right)_{t=0^+} = m_1 / R_\mu$$

Obviously the maximum value of μ is the one that maximizes R_μ and by comparison with (II.16) it is seen that the escape rate provides an upper bound to the nucleation rate enabling us to say that proving that a state is a metastable state according to MP II in PL formalism is enough to prove that the Becker-Döring approximation to the nucleation rate is also small.

One of the main ideas used in the Becker-Döring treatment is the artificial removal of clusters reaching an specified size and replacing them with small droplets. This idea was generalized by Penrose and Lebowitz[30] to more general systems improving on the corresponding restricted ensemble and making it possible to derive formulae for calculating nucleation rates from first principles.

The method can be applied to any system with a discret set of microscopic states in which its dynamics has the form of a Markov process.

Denoting by P_i the probability that the system is in the microscopic state i at time t, the rate of change of $P_i(t)$ is given by the master equation

$$\frac{d}{dt}P_i(t) = \sum_j (W_{ij}P_j(t) - W_{ji}P_i(t)) \qquad (II.20)$$

where W_{ij} is the transition probability from the state j to state i.

With e_i standing for the equilibrium probability of state i and assuming the validity for all i and j of the principle of detailed balance $W_{ij}e_j = W_{ji}e_i$ the only solution to (II.20) is

$$P_i = (\text{constant})\ e_i \qquad (II.21)$$

unless the states happen to split into different groups of states between which transitions are not allowed.

Now, if there is any metastable state, such a state must satisfy MP II and MP III, this amounts to say that in this case equation (II.20) can be approximated by

$$\frac{d}{dt}P_i(t) = \sum_j (W_{ij}P_j(t) - W_{ji}P_i(t)) \quad \text{if} \quad i \in \Gamma_M$$

$$P_i(t) = 0 \quad \text{if} \quad i \notin \Gamma_M \qquad (II.22)$$

where Γ_M is the special region in Γ (phase space) over which the restricted ensemble is defined.

Using the quantities $v_i(t)$ defined as $v_i(t) = P_i(t)/e_i$ it was proved that after a long time has elapsed the probabilities in an ensemble that started with any distribution over

will have the asimptotic form

$$P_i(t) \sim \text{const. } e^{-\lambda^{(0)} t} e_i v_i^{(0)} \qquad i \in \Gamma_M \tag{II.23}$$

with $v_i^{(0)}$ the eigenvector with eigenvalue $\lambda^{(0)}$ and $\lambda^{(0)}$ is the smallest eigenvalue of a suitable expression of the set of equations(*) (II.22).

This equation shows that once the transients (corresponding to fast "mechanisms") have died out, the behaviour of the system will be governed by the slow mechanism that is expressed by $\lambda^{(0)}$. If the region Γ_M corresponds to a metastable state then $\lambda^{(0)}$ can be interpreted as the rate of nucleation and therefore its value must be very small.

One more thing that can be said about $\lambda^{(0)}$ is that by using the Rayleigh-Ritz principle an upper bound on $\lambda^{(0)}$ can be found

$$\lambda^{(0)} \leq ((1/2) \sum_i{}' \sum_j{}' W_{ij} e_j (v_i - v_j)^2 + \sum_i{}' v_i^2 \sum_k{}'' W_{ki} e_i)(\sum e_i v_i^2)^{-1} \tag{II.24}$$

with Σ' meaning the sum goes over states in Γ_M and Σ'' the sum goes over states outside Γ_M. (In both cases the states are microstates). This inequality opens up the possibility of

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(*) This expression being $\lambda^{(r)} e_i v_i^{(r)} = \sum_j{}' G_{ij} v_j^{(r)}$ the sum going over the microscopic states in Γ_M and G_{ij} given by $G_{ij} = W_{ij} e_j - \delta_{ij} \sum_k W_{ki} e_i$ $(i,j \in \Gamma_M)$; $\lambda^{(r)}$ stands for the r-th eigenvalue of such equation(79).

relating $\lambda^{(0)}$ to the nucleation rate as calculated by means of the Becker-Döring set of equations.

Section 11. CAPOCACCIA, CASSANDRO, OLIVIERI. A DISCREET MODEL. CASSANDRO, OLIVIERI. A CONTINUOUS MODEL.

The contribution of Capocaccia, Cassandro and Olivieri[65] (CCO in what follows) is a sequel to the work done by Penrose and Lebowitz. Adapting the same three properties MP I, II, III given at the beginning of the introduct. they were able to prove the existence of metastable states in a special case of the Ising model and later on Cassandro and Olivieri[62] (CO from now on) showed that this also happens in a continuous model, the Widom and Rowlinson model[66] to be more specific.

To apprehend the importance of what follows it is necessary to keep in mind the result by Lanford and Ruelle[17] stating the impossibility of an analytic continuation of the equilibrium state to the metastable region in the case of short range forces.

The main point of the CCO and CO work is that in both cases -hey were dealing with short range interactions whereas in the Van der Waals-Maxwell treatement of the liquid-vapor transition the forces responsible for the appearence of the phase transition were of the long range type.

CCO considered a two-dimensional Ising spin system with nn(*) interactions and assumed the dynamics of the system was that of a markovian process.

The system is confined to a finite box Λ with boundary conditions given by the spin configurations $\underline{\zeta}$ outside Λ. The energy of the spin configuration $\underline{\sigma}$ inside Λ is

$$E_{\Lambda,\underline{\zeta}}(\underline{\sigma}) = -\frac{J}{2}\sum_{<k,k'>\in\Lambda}\sigma_k\sigma_{k'} - \frac{J}{2}\sum_{\substack{<k,k'> \\ k\in\Lambda \\ k'\notin\Lambda}}\sigma_k\zeta_{k'} - \frac{h}{2}\sum_{k\in\Lambda}\sigma_k \qquad (II.25)$$

where $J>0$ and $h/2$ is the external magnetic field.

The properties of the system can be described in terms of the infinite volumen limit of the spin correlation functions $\langle\sigma_A\rangle_{\Lambda,\underline{\zeta},h}$ and the free energy $F(\beta,h,\Lambda,\underline{\zeta})$. The expressions for these quantities in the finite system case are

$$\langle\sigma_A\rangle_{\Lambda,\underline{\zeta},h} = \frac{\sum_{\underline{\sigma}}\prod_{k\in A}\sigma_k \exp\{-\beta E_{\Lambda,\underline{\zeta}}(\underline{\sigma})\}}{\sum_{\underline{\sigma}}\exp\{-\beta E_{\Lambda,\underline{\zeta}}(\underline{\sigma})\}} \qquad (II.26)$$

$$F(\beta,h,\Lambda,\underline{\zeta}) = (1/|\Lambda|)\ln\sum_{\underline{\sigma}}\exp\{-\beta E_{\Lambda,\underline{\zeta}}(\underline{\sigma})\} = (1/|\Lambda|)\ln Z^{(\Xi)}(\Lambda,h) \qquad (II.27)$$

The configurations of the system were described in terms of contours, this technique having been developped by Minlos and Sinai(61).

(*) nn meaning all the particles interact with each other.

Let a configuration $\underline{\sigma} \in \Gamma(\Lambda)$ be given. By drawing a unit segment perpendicular to the centre of each bond having spins of opposite signs at its extreme lines can be formed, these lines separating regions where the spins are positive from regions where the spins are negative. In two dimensions and with fixed + or -(*) boundary conditions all the lines form closed plygons and it is proven that under this conditions the set of non interacting polygonals (or contours) separating opposite spins specifie a spin configuration that is unique.

Since these contours are a good analogy to a droplet they provide a nice physical image of what is happening in the system, and even more, the outer contours correlation functions obey a set of integral equations like those used by Kirkwood and Salsburg[15] (see Apendix), hence the importance of this description.

By outer contours we are refering to those contours not enclosed by other contours. The probability of finding a family of outer contours (ie. the outer contours distribution functions) is given by[65,68]

$$\rho_{\Lambda,h}(\gamma_1,\ldots,\gamma_n) = \frac{\prod_i \mu(\gamma_i,h) \sum'_{\{\tilde{\gamma}_i\}\subset\Lambda} \prod_{\tilde{\gamma}_i\in\{\tilde{\gamma}_i\}} \mu(\tilde{\gamma}_i,h)}{\Xi_\Lambda(\beta,h)} \qquad (II.21)$$

with

(*) + (or -) boundary conditions means that all the spins outside Λ which are nearest neighbors to spins in Λ are positive (or negative).

$$\mu(\gamma,h) = e^{-\beta J|\gamma| - \beta\frac{h}{2}|\mathcal{O}(\gamma)|}\,\xi^{-}(\gamma,h)$$

$$\Xi = \sum_{\{\gamma\}\subset\Lambda}{}' \prod_{\gamma\in\{\gamma\}} \mu(\gamma,h)$$

$|\gamma|$ is the length of the contour γ. $\xi^{-(+)}$ is the partition function for the region $\mathcal{O}(\gamma)$ enclosed by γ and - (or +) stands for the type of boundary conditions. The primed sum runs over all the contours compatible with $\gamma_1,\dots,\gamma_n$.

Minlos and Sinai[61] proved that for $h\geq 0$, $\beta>\beta''>\beta_c$ (where β_c is the critical temperature) there is a unique function over the families of compatible outer contours such that ($\text{II}.2\beta$) holds and the following can be proved to follow:

i) $f_h(\gamma_1,\dots,\gamma_n)$ is analytic in β and h if $h\neq 0$

ii) $f_h(\gamma_1,\dots,\gamma_n) \leq \exp\{-\beta J \sum_i^n |\gamma_i|\}$

iii) $|f_{\Lambda,h}(\gamma_1,\dots,\gamma_n) - \prod_{i=1}^n \chi_\Lambda(\gamma_i)\, f_h(\gamma_1,\dots,\gamma_n)| \leq$

$\exp\{-(\beta-\beta'')\frac{J}{2}\sum_i^n|\gamma_i|\}\,\phi(\Lambda,\beta)$

where

$$\chi_\Lambda(\gamma_i) = \begin{cases} 1 & \text{if } \mathcal{O}(\gamma_i)\subset\Lambda \\ 0 & \text{otherwise} \end{cases}$$

and

$$\lim_{\Lambda\to\infty} \phi(\Lambda,\beta) = 0$$

The spin correlation functions (expressed as sums of contour correlation functions) can therefore be proven to converge uniformely as $\Lambda\to\infty$ and their analyticy properties can be derived by standard methods[15].

In connection with the droplet model it is seen from

ii) of the preceding page that large contours are improbable if βJ is large, so that among the possible configurations in the grand canonical enesmble with + boundary conditions and $h \geq 0$ the most likely to appear, if βJ is large, are those with a large majority of + spins and small and rare "islands" of negative spins.

In order to define the metastable states it is necessary to eliminate the configurations associated with large contours ie. having big "droplets".

Let c be an integer and define Γ_M to be the subset of Γ given by

$$\Gamma_M = \{ \underline{\sigma} : |\mathcal{O}(\gamma)| \leq c^2 \ \forall \gamma \in \{\gamma\}_{\underline{\sigma}} \} \qquad (II.29)$$

where $\{\gamma\}_{\underline{\sigma}}$ is the collection of outer contours associated with the spin configuration $\underline{\sigma}$. c is arbitrary until now but the metastability requirement will provide a criterion for choosing it.

In accordance with the method deviced by PL we consider the state defined by the probability distribution

$$P_\Lambda(\underline{\sigma}) = \begin{cases} k \exp\{-\beta E_\Lambda(\underline{\sigma})\} & \text{if } \underline{\sigma} \in \Gamma_M \\ 0 & \text{otherwise} \end{cases} \qquad (II.30)$$

where k is a normalization constant.

By introducing the outer contours correlation functions $f^c_{\Lambda,h}$ for any set $\gamma_1, \dots, \gamma_n$ of compatible outer contours in Λ such that $|\mathcal{O}(\gamma_i)| \leq c^2$

$$f^c_{\Lambda,h}(\gamma_1,\dots,\gamma_n) = \frac{\prod_i \mu(\gamma_i,h) \sum'_{\{\tilde\gamma\}\subset\Lambda} |\mathcal{O}(\tilde\gamma)|<c^2 \prod_{\tilde\gamma\in\{\tilde\gamma\}} \mu(\tilde\gamma,h)}{\Xi^c_\Lambda(\beta,h)} \qquad (II.31)$$

where

$$\Xi^c_\Lambda(\beta,h) = \sum_{\{\gamma\}\subset\Lambda,\ |\mathcal{O}(\gamma)|\leq c^2} \prod_{\gamma\in\{\gamma\}} \mu(\gamma,h)$$

it was possible to prove the existence of $f^c_{\Lambda,h}$, and that for $\beta > \beta'' > \beta_c$, $h<0$ and $c < 4(\beta J - 2\alpha)/\beta|h|$ with $\alpha \geq \ln 6$ the following properties hold:

i)^c $f^c_h(\gamma_1,\dots,\gamma_n) = 0$ $\forall\gamma$ such that $|\mathcal{O}(\gamma)| > c^2$

ii)^c $f^c_h(\gamma_1,\dots,\gamma_n) \leq \exp\{-2\alpha \sum_i^n |\gamma_i|\}$

iii)^c $|f^c_{\Lambda,h}(\gamma_1,\dots,\gamma_n) - \prod_i^n \chi_\Lambda(\gamma_i) f^c_h(\gamma_1,\dots,\gamma_n)| \leq e^{-\alpha\sum_i^n|\gamma_i|} G(\beta,\Lambda)$

Where $\chi_\Lambda(\gamma)$ is the characteristic function for the outer contour γ and $\lim_{\Lambda\to\infty} G(\beta,\Lambda) = 0$ for any set $\{\gamma\}$.

iv)^c $|f^c_h(\gamma_1,\dots,\gamma_n) - \prod_i^n \chi^c(\gamma_i) f(\gamma_1,\dots,\gamma_n)| \leq e^{-\alpha\sum_i^n|\gamma_i|} B(\beta,h,c)$

Where $\chi^c(\gamma) = \begin{cases} 1 & \text{if } |\mathcal{O}(\gamma)| < c^2 \\ 0 & \text{otherwise} \end{cases}$

and $B(\beta,h,c) \to 0$ as $h\to 0^-$, $c\to\infty$ if $c|h| < 4(\beta J - 2\ln 6)$

We can see that these properties reproduce those satisfied by the contour correlation functions in the equilibrium case. A point to notice is that by considering any sequence of c's such that $c \to \infty$ as $h \to 0^-$, we get $\rho_h^c \to \rho$ as $h \to 0^-$ (provided $\alpha \geq 2 \ln 6$) and therefore it is impossible to define, on purely static grounds, a unique sequence of states approaching the equilibrium state as $h \to 0^-$ since there are a large number of such sequences exhibiting the property. In contrast with the Van der Waals-Maxwell theory where the isotherm in the metastable region was the analytic continuation of the equilibrium isotherm, in the case of short range forces a less defined prescription is achieved.

CCO proved the following theorem which summarize the static properties of the restricted ensemble. Given an Ising spin system with nn interactions of strength $J/2 > 0$ and external magnetic field $\frac{h}{2} < 0$, contained in a box Λ with $+$ boundary conditions, call Γ_M the spin configuration subset defined in (II.29) and let $S_{c,\Lambda}$ be the state defined by the probability distribution (II.30).

If $Z^+_c(\Lambda, h)$ is the partition function sum over Γ_M and $\langle \sigma_A \rangle^c_{\Lambda,h}$ (*), $A \subseteq \Lambda$ the related spin correlation functions when $\beta > 2 \ln 6 / J$, $c < 4(\beta J - 2 \ln 6)/\beta |h|$ then

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(*) The limit of the magnetization can be expressed as $\langle \sigma_0 \rangle^c_h = 1 + \sum_{\gamma : 0 \in \theta(\gamma)} \rho^c_h(\gamma) \langle \sigma_0 - \rangle_{\theta(\gamma)} - h$ -with the c in $\langle \sigma_0 \rangle^c_h$ and ρ^c_h meaning we are restricted to configurations where $|\theta(\gamma)| \leq c^2$ for all $\gamma \in \{\gamma\}$

a) The following limits exist and are finite

$$F^c(\beta, h) = \lim_{\Lambda \to \infty} (1/|\Lambda|) \ln Z_c^+(\Lambda, h)$$

$$\langle \sigma_A \rangle_h^c = \lim_{\Lambda \to \infty} \langle \sigma_A \rangle_{\Lambda, h}^c$$

b) The infinite volume correlation functions have cluster properties .

c) The central limit theorem holds for the magnetization and the energy.

d) Consider a sequence of c's such that $c \to \infty$ as $h \to 0^-$ (and $c|h| \leq \frac{4}{\beta}(\beta J - 2 \ln 6$) then

$$\lim_{h \to 0^-} \langle \sigma_A \rangle_h^c = \langle \sigma_A \rangle_{+,0}$$

$$\lim_{h \to 0^-} F^c(\beta, h) = F(\beta, 0)$$

where $\langle \sigma_A \rangle_{+,0}$ and $F(\beta, 0)$ are the corresponding quantities at equilibrium.

e) If $Z^+(\Lambda, h)$ is the partition function over the full equilibrium ensemble, the following limit holds

$$\lim_{\Lambda \to \infty} Z_c^+(\Lambda, h) / Z^+(\Lambda, h) = 0$$

With respect to the dynamical properties of the state defined by (II.30) it was assumed that the time evolution was governed by the master equation

$$\frac{\partial}{\partial t} P_\Lambda(\underline{\sigma}; t) = \sum_{\underline{\sigma}'} \{ W_\Lambda(\underline{\sigma}, \underline{\sigma}') P_\Lambda(\underline{\sigma}', t) - W_\Lambda(\underline{\sigma}', \underline{\sigma}) P_\Lambda(\underline{\sigma}, t) \} \quad (II.32)$$

where $P_\Lambda(\underline{\sigma}, t)$ is the probability distribution over the configuration in Λ at time t. $W_\Lambda(\underline{\sigma}', \underline{\sigma})$ is the transition probability from configuration $\underline{\sigma}$ to $\underline{\sigma}'$; detailed balance was assumed and also the existence, for any pair $\underline{\sigma}$ and $\underline{\sigma}'$, of a sequence $\underline{\sigma}', \underline{\sigma}^2, \ldots, \underline{\sigma}^n$ of configurations such that $\underline{\sigma}' \equiv \underline{\sigma}, \ldots, \underline{\sigma}^n = \underline{\sigma}'$ and $W_\Lambda(\underline{\sigma}^{i+1}, \sigma^i) \neq 0 \quad i = 1, \ldots, n-1$

The "escape rate" $\lambda(t)$ was defined as

$$\lambda \Gamma_M = -\frac{d}{dt} P(\Gamma_M, t) \qquad (II.33)$$

An argument based in Liouiville's theorem[10] shows that $\lambda(0) > \lambda(t) \; \forall \; t$ then with the help of this result the following theorem was proved:

Assuming that the system is in the state $S_{c,\Lambda}$ at $t=0$ then for any Λ, $P(\Gamma_M, t)$ is monotonic decreasing and $\frac{d}{dt} P(\Gamma_M, t)$ is a monotonic increasing function of t. With the escape rate λ defined as in (II.33) and with $\beta > 2\ln 6/J$ $c \leq 4(\beta J - 2\ln 6)/\beta|h|$, the following inequality holds:

$$F_1(\beta, h, c)\, e^{-4\beta J c + \beta m^*(\beta)|h| c^2 (1 + o(\partial\Lambda/|\Lambda|))} \leq \lambda \Gamma_M / |\Lambda| \leq$$

$$F_2(\beta, h, c)\, e^{-(\beta J - \ln 3) 4c + \beta |h| c}$$

where $m^*(\beta)$ is the equilibrium magnetization at $h = 0^+$ and F_1 and F_2 are bounded positive functions.

It is seen that the escape rate can be made as small as desired, hence providing the evidence for MPII to be satisfied.

These two theorems reproduce the phenomenology of a metastable state. Both the static and dynamic properties of $S_{c,\Lambda}$ are coupled in a rigorous way and for a discrete system provide an extension, for short range forces, of some of the results already known to hold in the long range forces case.

Cassandro and Olivieri[62] (CO) carried on this work and studied a continuous model known as the Widom and Rowlinson model[66] which is a continuous model with two kinds of particles A and B having a hard core repulsion of range $\bar{1}$ between unlike-particles and no interaction between like-particles The only parameters of the model are the activities z and and the characteristic distance $\bar{1}$.

This model can simulate a liquid-vapor transition by taking the B particles to be invisible and besides, this is the only short range force continuous model for which a phase transition has been rigorously proved to exist.

Once again Minlos and Sinai's results[61] with the contours description proved their usefulness. To this effect the construction of Ruelle[63] was taken as the starting point:

Let Λ be a box containing a square lattice of $d \times d$ squares with $d=\bar{1}/3\sqrt{2}$ ($\bar{1}$ is the diagonal of a $3d \times 3d$ square) The number of squares will then be given by $N = |\Lambda|$ $(d \times d)$ The boundary condition being that the strip composed by the first four squares adjacent to the boundary of Λ cannot contain b particles (A-boundary conditions). Now, by shading

all the 3d × 3d squares centered on the little squares containing at least one B particle and by taking the union of these shaded areas, the boundary of such union will be a polygon of various edges "self avoiding" closed contours. By considering only the outer ones a chain C is defined as the smallest set of outer contours such that if two outer contours have a distance less than $8\bar{l}/3\sqrt{2}$ they belong to the same chain. As in the preceding cases, two chains will be said to be compatible if they can appear in the same configuration as disjoint chains.

In terms of chains the grand canonical partition function can be written as[64]

$$\Xi(\Lambda) = \sum_{\{c_1,\dots,c_s\}}{}' \prod_i^s \frac{\Xi(\tilde{\mathcal{O}}(c_i))}{\Xi_0(\tilde{\mathcal{O}}(c_i))} \Xi_0(\Lambda) \qquad (II.34)$$

where the primed sum goes over all the collections $\{c_1,\dots,c_s\}$ of compatible chains in Λ, $\mathcal{O}(c)$ is the disconnected region with C as boundary and $\tilde{\mathcal{O}}(c)$ will be $\mathcal{O}(c)$ plus the strip containing all the squares at a distance less than $\bar{l}$ from the little squares internal to the outer contours belonging to C.

$\Xi(\tilde{\mathcal{O}}(c))$ is the partition sum over all the A B configurations in $\tilde{\mathcal{O}}(c)$ compatible with the presence of the chain C. Ξ_0 is the partition sum of a free gas of A particles.

The m-chain correlation function reads[64]

$$f_\Lambda(c_1,\dots,c_m) = [\Xi(\Lambda)]^{-1} \sum_{c_1^\circ,\dots,c_s^\circ} \prod_i^s \cdot \frac{\Xi(\tilde{\omega}(c_i))}{\Xi_0(\tilde{\omega}(c_i))} \Xi_0(\Lambda) \quad (\text{V}.35)$$

and it is proven that when $z_A = z_B = z$ is large enough

$$f_\Lambda(c_1,\dots,c_m) \leq \exp\{-\alpha \sum_{i=1}^m |c_i|\} \quad (\text{V}.36)$$

where $\alpha = z\mathcal{R}^2/72$ showing a result similar to the one obtained in the discreet case[65]: long chains (contours in the previous case) are not likely to appear in the high activity region.

The functions $f_\Lambda(c_1,\dots,c_m)$ also satisfy a set of integral equations like those of Kirkwood and Salzburg allowing us therefore to prove, for values of z high enough, the analyticity and cluster properties together with its convergence in Λ [15].

In order to discriminate configurations associated to chains of a given size the procedure is the same as in the discrete case treated by CCO. The region Γ_M is defined as

$$\Gamma_M = \{\eta : |\theta(c)| \leq c_*^2 \quad \forall c \in \{c\}_\eta\} \quad \text{V}.37$$

where $\{c\}_\eta$ is the collection of outer contours associated to the A-B particle configuration η and c^* is a constant that will be determined later by the metastability requirements. CO proved that in order to have an image typical of an A-rich phase, with z_A sufficiently high, then c_* has an upper bound given by $c < 1/12^3 h = (1/12^3) \ln(z_B/z_A)$

Then a state is defined as

$$\rho_1(\eta) = \begin{cases} K Z_A^{N_A(\eta)} Z_B^{N_B(\eta)} & \text{if } \eta \in \Gamma_M \\ 0 \quad \text{otherwise} \end{cases} \qquad \text{II.38}$$

Rephrasing known arguments leads the "escape rate" to be defined as

$$\lambda = \left.\frac{d P(t)}{dt}\right|_{t=0^+} = \lim_{\delta t \to 0^+} \sup \frac{P(\delta t)}{\delta t} \qquad \text{II-39}$$

Then a suitable mathematical definition of "critical boundary" is given, roughly meaning the set of segments such that if a B particle crosses one of them, the resulting configuration belongs no more to Γ_M .

Let E_b be the following event: a B particle is approaching a given segment b at a distance less than δt times its component $\bar{l}$ of velocity perpendicular to b . And let F_b stand for the event : at time zero the configuration of the system has a non empty critical boundary containin b.

With this in hand $P(\delta t)$ was given by

$$P(\delta t) = \sum_{b \in \mathcal{B}} prob\,(E_b, F_b) + o(\delta t^2) \qquad \text{II.40}$$

where $prob\,(E_b, F_b)$ is the joint probability of E_b and F_b evaluated in the restricted ensemble and $\mathcal{B}$ is the set of all b's in Λ that can be crossed by a B particle.

$o(\delta t^2)$ is the contribution to $P(\delta t)$ of all sort of events

involving more than one particle.

An upper bound to (II.39) is found to be

$$\lambda \leq G(Z_A, Z_B)\, e^{-4\mu^2/v} \qquad (II.41)$$

where

$$G \propto Z_B\, e^{-(Z_A+Z_B)+\alpha}$$

$$4\mu \propto hc\alpha$$

$$v \propto 4hq$$

$$\alpha = Z_A d^2/4$$

$$h = \ln(Z_B/Z_A)$$

From (II.41) it is seen that the bound decreases exponentially in Z_A when h is small enough showing that when Z_A and Z_B are high and at the same time close enough, the escape rate can be made very small.

CHAPTER III. CLUSTER DISTRIBUTIONS. THE REPLACEMENT FACTOR.

Introduction.

The main purpose of this chapter is to obtain, for a continuous classical system, an approximation to the expected number of N-particle clusters m_N which will be formally identical to expression $(\mathrm{II}.8)$. This approximation was essential to obtain, in the discrete case to which $(\mathrm{II}.8)$ applies, a rigorous version of the Boltzmann-factor approximation $e^{-\beta \Delta F_N}$ to m_N normally used in nucleation theory.

Since clusters play a vital role in the obtention of an expression for m_N in our classical system, we begin the chapter with the definitions of what our continuous classical system is and then we proceed to define clusters in terms of the elements forming our system. Since any finite or infinite configuration of particles corresponds to a distribution of clusters then we can expect that something like a grand canonical cluster distribution can be obteined by starting from the grand canonical particle distribution on a bounded region. This is done in Sections 2 and 4 . Inmediately we find upper and lower bounds to the log of the distribution function. These bounds are then used to obtain an approximation to m_N.

In the last section we reproduce for a continuous model the result obtained by Penrose and Lebowitz for a lattice gas. This result states that if the replacement factor Γ is made equal to m^{-1} then m_N is in agreement with the approximation to m_N used in nucleation theory. This result suggest that at low densities m^{-1} is a good approximation to Γ .

The particle space.

Let S be the d-dimensional Euclidean space $\mathbb{R}^d$ $(d \geq 1)$ and $\mathcal{B}$ the σ-field of Borel sets in S. In addition, Γ will stand for all the bounded $\Lambda \subset S$. A measure m (a Lebesgue measure is sufficient for the problem under consideration) is defined on $(S, \mathcal{B})$ with the specification that $m(\{\vec{x}\}) = 0$ for all $\vec{x} \in S$.

The configuration space.

In order to define this space a counting measure (in general it can be an integer valued Radon measure on $(S, \mathcal{B})$) is introduced, this being expressed through the formula

$$\omega(\Lambda) \equiv \text{card}\{x \in \Lambda\} \qquad (\Lambda \in \Gamma) \qquad \text{III}.1$$

Since the configurations of interest are those (with particles being indistinguisible) that are locally finite, ie. the number of particles in Λ is finite, then the configuration space Ω will be taken to be

$$\Omega = \{\omega \subset S : \omega(\Lambda) < \infty \quad \forall \Lambda \in \Gamma\}$$

with $\omega(\Lambda)$ as in (III.1). Here ω stands both for the configuration on Λ and the counting measure. The context will make plain which meaning is being used.

States on Ω

A probability measure μ on $(\Omega, \mathcal{F})$ is called a state. As usual, $\mathcal{F}$ is the σ-algebra of subsets of Ω. In our case the probability measure used is the one corresponding to the grand canonical distribution.

The particle interaction.

Let Ω_Λ° be the configuration space resticted to Λ with the "o" symbol meaning $V(\circ) = 0$. By interaction potential will be understood a measurable function V on $\Omega_f = \cup \{\Omega_\Lambda^\circ ; \Lambda \in \Gamma\}$ such that the following requirements are satisfied

V 1 Stability.

There exists a constant $B \geq 0$ such that

$$V(\omega) \geq -B\omega \qquad \forall \omega \in \Omega$$

V 2 Finiteness.

There are a norm $\|\cdot\|$ on S such that $\{x \in S : \|x\| < 1\}$ is convex and a constant $r \geq 0$ such that $V(\omega) < \infty$ if and only if $\omega \in \Omega_r$, where $\Omega_r = \{\omega \in \Omega : \|x - y\| > r, x, y \in \omega\}$

When $r > 0$ the interaction potential V is called a hard core potential and for simplicity the particles are supposed to be balls of radius $r/2$.

V 3 Finite range.

There exists $R > 0$ such that for all $\omega \in \Omega$ and all $\Lambda \in \Gamma$ such that $\omega_{S \setminus \Lambda} \in \Omega_r$ we have

whenever $\bar{\Lambda} \subset \Delta \in \Gamma$

In here $\bar{\Lambda} = \Lambda \cup \partial\Lambda$ and $\partial\Lambda$ is the set of all $x \in S \setminus \Lambda$ whose euclidean distance from Λ is not greaterthan R. In other words, one particle interacts with another if and only if the distance between them is less than R.

According to the case under consideration V will be given in terms of a pair potential, meaning there is a measurable symmetric function ϕ on $S \times S$ such that for all $\omega \in \Omega_f$

$$V(\omega) = \frac{1}{2} \sum_{x,y \in \omega, x \neq y} \phi(x,y) = \frac{1}{2} \sum_{x,y \in \omega, x \neq y} \phi(\|x-y\|)$$

ϕ is assumed to have the properties

i) $\phi(\ldots) \geq -c$ for some constant $c \geq 0$

ii) $\phi(\ldots) < \infty$ for all $x \in S$ under consideration in V2

iii) There exists $R > 0$ with $\phi(x) = 0$ for $|x| > R$

CLUSTERS

The concept of clusters arises naturally from the visualization of the system of particles as subdivided into sets which at a certain instant of time have a precise localization in space. Generally speaking this spatial distribution is going to determine the strength of the interaction between particles thus providing a criterion for how to choose the most probable configurations. Furthermore, sometimes attention is directed

to particular regions of space hence the importance of obtaining the information required by means of the objects in a vecinity of the region in question. This kind of situation appears in the case of finite range potential where the concept of cluster can be inmediately introduced. More precisely, a set of particles is said to constitute a cluster if the graph obtained by joining interacting particles is connected. In this case being "connected" means:

a) that none of the particles forming a cluster is a nearest neighbor of a particle associated to another cluster and

b) if the cluster is split into two subsets A and B then at least one of the particles of A (or B) is a nearest neighbor of a particle of B (or A), ie. if the distance of at least one particle of one set from a particle of the other set is less then R .

This definition is capable of more than one exact mathematical expression (Penrose and Lebowitz[30], Murmann[80], Cassandro et al[62,65], Ruelle[63], Minlos and Sinai[61], Mayer[37,59]) . The choise of a particular definition is dependent on what the model is and what sort of formula is most suitable to our purposes. In a way that that resembles the construction of the Mayer expansion[59], cluster functions will be defined and in terms of such functions the physical clusters will be given. Since every finite or infinite particle configuration corresponds to a distribution of clusters therefore it seems reasonable to expect that something like

a grand canonical cluster distribution can be derived by starting from the grand canonical particle distribution in a bounded region. This will prove to be the case if a suitably defined measure and cluster's hard core potential are introduced.

Let Δ be the cluster function mentioned in the above paragraph. As its name suggests it is an indicator function. However, this is not enough to provide a workable expression for Δ and since the presence or absence of a cluster is ultimately determined by the manner the particles are distributed in space one expects that in order to define Δ one should resort explicitly to the particle distribution. To this end let $h : S \times S \longrightarrow \{0,1\}$ be given by

$$h(x,y) = \begin{cases} 1 & \text{for } |x-y| > R \\ 0 & \text{otherwise} \end{cases} \qquad (\text{III}.2)$$

where $x, y \in S$ and R is a constant. This $h(x,y)$ will permit us to handle the case of more than two particles. This is done by generalizing the notation in III.2 to

$$h(x_1,\dots,x_n; y_1,\dots,y_m) = \prod_{i=1}^{n} \prod_{j=1}^{m} h(x_i; y_j) \qquad (\text{III}.3)$$

with $x_1,\dots,x_n$, $y_1,\dots,y_n \in S$. This function h takes the value 1 when the particles occupying the positions labeled with the x's are separated by a distance no less than R from all the particles at the positions labeled with the y's. If this is not the case then h equals 0. This happens to be the same function h used in the Mayer expansion.

No problem should arise in distinguishing the h on the left hand side of the equation and whose domain of definition is $\underbrace{S \times \ldots \times S}_{n+m \text{ times}}$ from the h on the right-hand side.

Finally, the cluster function $\Delta : \Omega \to \{0,1\}$ is defined for any $x_1, \ldots, x_\ell \in \omega$ to read

$$\Delta(x_1, \ldots, x_\ell) = \sum_{G \in \Gamma_\ell} \left[\prod_{(i,j) \in G} 1 - h(x_i, x_j) \right] \prod_{(a,b) \notin G} h(x_a, x_b)$$

where Γ_ℓ is the set of all connected graphs G with vertices $1, \ldots, \ell$.

This gives a way of introducing the space of clusters $\mathcal{C}_\ell$ ie. the space of the ℓ-particle clusters. In terms of Δ it is expressed as

$$\mathcal{C}_\ell = \{(x_1, \ldots, x_\ell) : \Delta(x_1, \ldots, x_\ell) = 1\} \subset \Omega$$

In addition, if by $\mathcal{C}$ we denote the space of all clusters then

$$\mathcal{C} = \sum_{\ell=1}^{\infty} \mathcal{C}_\ell$$

where $\sum_{\ell=1}^{\infty}$ denotes the topological sum of the $\mathcal{C}_\ell$'s .

The aim in introducing clusters is to try to select sets of particles with the property that elements of one set will only interact with the other elements of the same set, thus implying clusters can be pictured as particle-like sets

and, if the fugacity is small enough (hence the density is also small) then the system will look like a "gas" of clusters whose only interaction is one preventing the overlapping of clusters. The formalization of this picture can be done again through an exclusion function H in analogy to the h introduced before.

Let $\sum_{k=0} \mathcal{C}_k$ be the space of all finite cluster configurations and $H : \{\sum_{k=0}^{\infty} \mathcal{C}_k\} \to \{0,1\}$ be defined as

$H|_{\mathcal{C}_0} \equiv 1 \qquad H|_{\mathcal{C}_1} \equiv 1$

$$H((x_1,\dots,x_n),(y_1,\dots,y_m)) = h(x_1,\dots,x_n,y_1,\dots,y_m) \qquad (\text{III}.4)$$

where $\mathcal{C}_0$ is the empty cluster configuration associated to the empty particle configuration. If clusters are designated by capital letters $X_1, X_2, \dots$

$$H(X_1,\dots,X_k) = \prod_{1 \le i < j \le k} H(X_i, X_j) \qquad (\text{III}.5)$$

This amounts to thinking about H as related to a hard core potential which is part of the interaction between clusters.

CLUSTER DISTRIBUTION

The first problem encountered in attempting to describe the behaviour of the system of clusters is the specification of the partition function which will deal with such objects. Due to the correspondence between particle and cluster con-

figurations it is natural to expect that by means of suitable definitions relating particles and clusters, the distributions for the later can be derived from the distributions of the former.

Before going any further with the distribution functions some additional definitions seem pertinent.

Every finite set $\gamma = \{ i_1, \ldots, i_\ell \}$ of non-negative integers will be used as an abbreviation for $\Delta (x_{i_1}, \ldots x_{i_\ell})$ so that afterwards it will read

$$\Delta (\gamma) = \Delta (x_{i_1}, \ldots x_{i_\ell})$$

Once the particles are subdivided into clusters the following relation holds[81]

$$\sum^{(n)} \frac{1}{k!} \Delta(\gamma_1) \ldots \Delta(\gamma_k) \prod_{1 \le i < j \le k} h(\gamma_i ; \gamma_j) = 1 \qquad (III.6)$$

where $\sum^{(n)}$ is a sum over all ordered partitions $\{ \gamma_1, \ldots, \gamma_k \}$ of $\{ 1, \ldots, \ell \}$ into an arbitrary number of disjoint non-empty subsets. In other words, equation (III.6) is a sum over all possible ways of forming clusters by means of arbitrarily partitioning the set of particles in the system. The $k!$ appearing in the equation is to avoid repetitions of those partitions of $\{ 1, \ldots, k \}$ for which the γ_i clusters have only been re-labelled.

Each one one of the terms of the sum corresponds to a

possible cluster configuration, therefore it is valid to write

$$\eta = \omega(\gamma_1, \ldots, \gamma_k) = \omega(\gamma_1) + \ldots + \omega(\gamma_k)$$

where ω is the function defined in III.1 ie. $\omega(\gamma_i)$ stands for the number of particles in the cluster γ_i.

For the interaction energy V of the system a similar relation holds:

$$V(\gamma_1, \ldots, \gamma_k) = V(\gamma_1) + \ldots + V(\gamma_k)$$

This result comes from the fact that pairs of particles contribute to the energy only if both particles belong to the same cluster. Now we can proceed to study the grand canonical distribution function.

Let $\Lambda \in \mathcal{B} \cap \Gamma$ (ie. Λ is a bounded Borel set), $\beta > 0$ as usual is the inverse temperature parameter and $z > 0$ is the activity expressed as $e^{\mu/kT}$. Then the grand canonical partition function $\Xi(\Lambda, z, \beta)$ is given as

$$\Xi(\Lambda, z, \beta) = \sum_{\eta=0}^{\infty} n!^{-1} z^n \int \ldots \int_{\Lambda} dx_1 \ldots dx_N \exp\{-\beta V(x_1, \ldots, x_n)\} \qquad (III.9)$$

From (III.6) and (III.8) we get

$$\exp(-\beta V(x_1, \ldots, x_n)) = \sum^{(n)} k!^{-1} \Delta(\gamma_1) \exp\{-\beta V(\gamma_1)\} \ldots \Delta(\gamma_k) \exp\{-\beta V(\gamma_k)\} \times$$

$$\times \prod_{1 \le i < j \le k} h(\gamma_i; \gamma_j)$$

which if substituted in (III.9) gives

$$\Xi(\Lambda,z,\beta) = 1 + \sum_{n=1}^{\infty} n!^{-1} z^n \int\cdots\int_{\Lambda^n} dx_1 \cdots dx_n \sum^{(n)} k!^{-1} \times$$

$$\times \Delta(\gamma_1) \exp\{-\beta V(\gamma_1)\} \times \cdots \times \Delta(\gamma_k) \exp\{-\beta V(\gamma_k)\} \prod_{1\le i<j\le k} h(\gamma_i;\gamma_k)$$

(III.10)

For the sake of clarity lets write $\omega(\gamma_i) = |\gamma_i|$ so that $|\gamma_i|$ is still the number of particles in the cluster γ_i. With this notation and since the way n particles can be saparated into k sites is $n!/|\gamma_1|!\cdots|\gamma_k|!$ eqn. (III.10) is transformed into

$$\Xi(\Lambda,z,\beta) = 1 + \sum_{n=1}^{\infty} z^n \int\cdots\int_{\Lambda^n} dx_1 \cdots dx_n \; \frac{\Delta(\gamma_1)}{|\gamma_1|!} \exp\{-\beta V(\gamma_1)\} \times$$

$$\times \frac{\Delta(\gamma_k)}{|\gamma_k|!} \exp\{-\beta V(\gamma_k)\} \prod_{1\le i<j\le k} h(\gamma_i;\gamma_j)$$

and then

$$\Xi(\Lambda,z,\beta) = 1 + \sum_{n=1}^{\infty} z^n \int\cdots\int_{\Lambda^n} \Sigma'^{(n)} \frac{\Delta(\gamma_1)}{|\gamma_1|!} \exp\{-\beta V(\gamma_1)\} \prod_{2\le j\le k} (\gamma_1;\gamma_j)\, dX_{\gamma_1}$$

$$\times \frac{\Delta(\gamma_k)}{|\gamma_k|!} \exp\{-\beta V(\gamma_k)\} \prod_{1\le j\le k-1} h(\gamma_k,\gamma_j)\, dX_{\gamma_k} \qquad (III.11)$$

where dX_{γ_i} stands for the dx's corresponding to the particles in cluster γ_i and the prime on the sum indicates that it only extends over ordered partitions of $\{1,\ldots,n\}$.

Consider now a measure μ defined on φ by

$$d\mu_{\varphi_l}(x_1,\ldots,x_l) = l!^{-1} z^l \Delta(\gamma=\{x_1,\ldots,x_l\}) \exp\{-\beta V(x_1,\ldots,x_l\}\, dX_\gamma$$

(III.12)

and the set $\Lambda_* = \{ \underline{X} = (x_1, \ldots, x_l) : x_i \in \Lambda \quad i = 1, \ldots, l ; \; l \geq 1 \}$

Rewriting the last expression for $\Xi(\Lambda, z, \beta)$ in terms of eqn (III.11) we get

$$\Xi(\Lambda, z, \beta) = \sum_{k=0}^{\infty} k!^{-1} \int \ldots \int_{\Lambda^k} H(\underline{X}_1, \ldots, \underline{X}_k) \, d\mu(X_1) \ldots d\mu(X_k) \tag{III.13}$$

where H is as in eqn. (III.4) and eqn. (III.5) and for every Borel set $A \in \mathcal{C}$, $\textcircled{H}$ is defined by

$$\textcircled{H}(A, z, \beta) = \sum_{k=1}^{\infty} k!^{-1} \int \ldots \int_{A^k} H(\underline{X}_1, \ldots, \underline{X}_k) \, d\mu(X_1) \ldots d\mu(X_k)$$

Inasmuch as eqn. (III.13) resembles a grand canonical partition function for non-overlaping clusters it can be used to set the probability distribution for clusters. There is some ambiguity in the choice of the probability measure on $\sum_{k=0}^{\infty} \Lambda_*^k$ as a cluster distribution; this is due to the different manner of labelling the clusters for each fixed particle configuration. Following Mürmann[80] we take

$$\frac{H(\underline{X}_1, \ldots, \underline{X}_k) \, d\mu(X_1) \ldots d\mu(X_k)}{\textcircled{H}(\Lambda_*, z, \beta)}$$

which formally is a grand canonical distribution, the only thing done being the replacement of the Lebesgue measure by the measure μ and the introduction of the hard-core potential of cluster configurations.

The validity of the formula is restricted to small small enough value of z where the radius of convergence of μ (being a power series in z. See Mürmann[80]) does not depend on Λ and is strictly positive.

AN UPPER BOUND TO $\log \Xi(\Lambda, z, \beta)$.

Having shown how a grand canonical cluster distribution can be constructed we turn back to eqn. (III.11) and redefine terms in a way more suitable to our purposes.

Let Z_n be

$$Z_n = \int_{\Lambda^n} \cdots \int_{\Lambda^n} dX_n \frac{\Delta(x_1,\ldots,x_n)}{n!} \exp\{-\beta V(x_1,\ldots,x_n)\} \qquad (III.14)$$

Substituting eqn. III.14 in eqn. III.11 we obtain

$$\Xi(\Lambda,z,\beta) \leq 1 + \sum_{n=1}^{\infty} z^n \left\{ \sum_{\{\gamma\}}{}'^{(n)} \frac{1}{k!} \left(\prod_{1\leq i\leq k} Z_{|\gamma_i|} \right) \right\}$$

$$= 1 + \sum_{n=1}^{\infty} \left\{ \sum_{\{\gamma\}}{}'^{(n)} \frac{1}{k!} \left(\prod_{1\leq i\leq k} z^{|\gamma_i|} Z_{|\gamma_i|} \right) \right\}$$

$$= 1 + \sum_{\{\gamma\}} \left(\prod z^{|\gamma_i|} Z_{|\gamma_i|} \right) \qquad (III.15)$$

with the sum $\sum_{\{\gamma\}}{}'^{(n)}$ going over all ordered partitions of n particles and $\sum_{\{\gamma\}}$ going over all ordered partitions that can be made with an arbritary number of disjoint subsets and

arbitrary number of particles. The "1" in the sum corresponds to the case when no clusters are present.

Since all the terms in the sum are positive, an upper bound to $\Xi(\Lambda, z, \beta)$ is given by

$$\Xi(\Lambda, z, \beta) \leq \prod_{\{\gamma\}} (1 + z^{|\gamma_i|} Z_{|\gamma_i|})$$

Our interest will be centered around an expression involving the thermodynamic potential corresponding to $\Xi(\Lambda, z, \beta)$ and upper bounds to this potential can be found by using the above inequality. Hence

$$\log \Xi(\Lambda, z, \beta) \leq \sum_{\{\gamma\}} \log (1 + z^{|\gamma_i|} Z_{|\gamma_i|})$$

and

$$\log \Xi(\Lambda, z, \beta) \leq \sum_{\{\gamma\}} z^{|\gamma_i|} Z_{|\gamma_i|} \qquad (III.16)$$

If we group this series according to the size of the cluster we get

$$\log \Xi(\Lambda, z, \beta) \leq \sum_{\{\gamma\}} z^{|\gamma_i|} \mathcal{Z}_{|\gamma_i|}$$

where

$$\mathcal{Z}(\Lambda, \beta) = \sum_{\{\gamma\}_{=|\gamma|=N}} Z_N \qquad (III.17)$$

Let Q_N be defined as

$$Q_N = \lim_{\text{large } \Lambda} \frac{1}{|\Lambda|} \mathcal{Z}_N(\Lambda, \beta) \qquad (III.18)$$

and let us assume Q_N exists in our case. This is a plausible assumption when $|\Lambda|$ is large enough compared to N, since in this case each cluster in the sum (III.14) is congruent

under translations to approximately $|\Lambda|$ other clusters. In other words $Z_N(\Lambda,\beta)$ is approximately proportional to $|\Lambda|$. Thus defined the Q_N can be interpreted as the internal partition function for clusters of N particles. A point worth mentioning is that the limit that defines Q_N is reached from below. This can be seen in eqn (III.17) : by putting together two regions of size $|\Lambda|$ the number of clusters that can be found is more than twice the number of clusters in a region of size $|\Lambda|$. This is due to the fact that in the region of size $2|\Lambda|$ besides the clusters appearing in the region Λ there will be new ones that can be formed through the union surface of the regions where two clusters of smaller size will join forming clusters of the desired size. So we get $Z_N(2\Lambda) \geq 2 Z_N(\Lambda)$ and in the same way it can be seen that if the sequence $\{i\Lambda\}$ is taken the limit is approached from below and $\frac{Z_N(\Lambda)}{|\Lambda|} \leq Q_N$

By combining (III.16), (III.17), and (III.18) we obtain:

$$\lim_{(\text{large }\Lambda)} \frac{1}{|\Lambda|} \log \Xi(\Lambda,z,\beta) \leq \lim_{(\text{large }\Lambda)} \frac{1}{|\Lambda|} \sum_{\{\gamma\}} z^N Z_N = \sum_{\{\gamma\}} z^N Q_N$$

ie.
$$\lim_{(\text{large }\Lambda)} \frac{1}{|\Lambda|} \log \Xi(\Lambda,z,\beta) \leq \sum_{\{\gamma\}} z^N Q_N \qquad (III.19)$$

with N standing for the number $|\gamma_i|$.

Hence, if z is small enough for the series $\sum_{\{\gamma\}} z^N Q_N$ to converge then this series provides an upper bound on $\lim_{(\text{large }\Lambda)} \frac{1}{|\Lambda|} \log \Xi(\Lambda,z,\beta)$ ie. on β times the pressure. This result will permit us to find an upper bound to the probability $p(c)$ that the cluster c is present in the system.

AN UPPER BOUND ON m_N.

The ℓ-point correlation function[15] $\rho_\Lambda(x)_\ell = \rho_\Lambda(x_1,\dots,x_\ell)$ is defined as the probability density (with respect to Lebesgue measure) for finding ℓ different particles at prescribed positions $x_1,\dots,x_\ell \in \Lambda$ and is given by

$$\rho_\Lambda(x)_\ell = \frac{1}{\Xi(\Lambda,z,\beta)} \sum_{n=0}^{\infty} \frac{z^{\ell+n}}{n!} \int_{\Lambda^n} dx_{\ell+1}\dots dx_{\ell+n} \cdot \exp\{-\beta V(x_1,\dots,x_{\ell+n})\}$$

and therefore the probability density for finding an ℓ-particle cluster, with the ℓ particles at prescribed positions is

$$\rho_\Lambda^\ell = \frac{1}{\Xi(\Lambda,z,\beta)} \frac{z^\ell}{\ell!} \Delta(x_1,\dots,x_\ell) e^{-\beta U(x_1,\dots,x_\ell)} \left\{ \sum_{N=0}^{\infty} \frac{z^N}{N!} \int\dots\int_\Lambda e^{-\beta U(\dots} \times h(X_1,\dots X_N)\, dX_N \right\}$$

and since $$\sum_{N=0}^{\infty} \frac{z^N}{N!} \frac{\int\dots\int_\Lambda e^{-\beta U(x_1,\dots,x_{\ell+n})} h(X_1,\dots,X_N)\, dX_N}{\Xi(\Lambda,z,\beta)} \le 1$$

it follows that

$$\rho_\Lambda^\ell \le \frac{z^\ell}{\ell!} \Delta(x_1,\dots,x_\ell) e^{-\beta U(x_1,\dots,x_\ell)} \qquad (III.20)$$

Now, let $P(c)$ stand for the probability that cluster c is present in the system and $P(\sim c)$ for the probability that cluster c is not present..

Given a configuration in which cluster c is present the removal of this cluster will leave us with a configuration with a probability greater than the original by the factor

$$\int \dots \int_\Lambda f_\Lambda^{\ell}(x)_\ell \, dx_1 \dots dx_\ell$$

ie.

$$P(\sim c) \geq \left[\int \dots \int_\Lambda f_\Lambda^{|c|} dx_1 \dots dx_\ell \right] P(c)$$

Adding $\left[\int \dots \int_\Lambda^{|c|} dx_1 \dots dx_\ell \right] P(\sim c)$ to both sides of this equation will produce

$$\left[\int \dots \int_\Lambda f_\Lambda^{|c|} dx_1 \dots dx_\ell \right] P(\sim c) + P(\sim c) \geq$$

$$\left[\int \dots \int_\Lambda f_\Lambda^{|c|} dx_1 \dots dx_\ell \right] (P(\sim c) + P(c))$$

and since $P(\sim c) + P(c) = 1$ then

$$P(\sim c) \left[\left(\int \dots \int_\Lambda f_\Lambda^{|c|} dx_1 \dots dx_\ell \right) + 1 \right] \geq \int \dots \int_\Lambda f_\Lambda^{|c|} dx_1 \dots dx_\ell$$

therefore

$$P(\sim c) \geq \frac{\int \dots \int_\Lambda f_\Lambda^{|c|} dx_1 \dots dx_\ell}{1 + \int \dots \int_\Lambda f_\Lambda^{|c|} dx_1 \dots dx_\ell}$$

and it follows that

$$P(c) \leq \frac{\int \dots \int_\Lambda f_\Lambda^{|c|} dx_1 \dots dx_\ell}{1 + \int \dots \int_\Lambda f_\Lambda^{|c|} dx_1 \dots dx_\ell} \leq \int \dots \int_\Lambda f_\Lambda^{|c|} dx_1 \dots dx_\ell$$

thus giving us an upper bound to $P(c)$, namely

$$P(\gamma) \leq \int \dots \int_\Lambda f_\Lambda^{|\gamma|} dx_1 \dots dx_\ell \leq$$

$$\leq \int \dots \int_\Lambda \frac{z^{|\gamma|}}{|\gamma|!} \Delta(x_1, \dots x_{|\gamma|}) e^{-\beta U(x_1, \dots, x_{|\gamma|})} dx_1 \dots dx_{|\gamma|}$$

(III.21)

where in the last inequality we made use of eqn. (III.20)

Now we can move to show that the expected number of N-particle clusters per unit volume, denoted by m_N, has an upper bound.

By definition

$$m_N = \frac{1}{|\Lambda|} \sum_{\gamma:\,|\gamma|=N} P(\gamma) \qquad (III.22)$$

so that by using the inequality (III.21)

$$m_N = \frac{1}{|\Lambda|} \sum_{\gamma:\,|\gamma|=N} P(\gamma) \leq \frac{1}{|\Lambda|} \sum_{\gamma:\,|\gamma|=N} \int\cdots\int_{\Lambda} \frac{z^N}{N!} \times$$

$$\times\ \Delta(x_1,\ldots,x_N)\, e^{-\beta U(x_1,\ldots,x_N)}\, dx_1 \ldots dx_N = \frac{1}{|\Lambda|} \sum_{\gamma:\,|\gamma|=N} z^N Z_N$$

$$= z^N Q_N$$

In short

$$m_N \leq z^N Q_N \qquad (III.23)$$

LOWER BOUNDS ON m_N.

Lebowitz and Penrose[60] derived a lower bound for m_N in the case of a lattice gas with attractive potential of finite range. This lower bound had the general form

$$z^N Q\,(1 + o|z|) \leq m_N$$

This result suggested that a similar inequality could be proved in the continuos case we are dealing with.

To show this is also valid in our case we start from the the expression for the probability of having N particles forming a cluster, ie. from

$$P_N = \frac{1}{\Xi(\Lambda, z, \beta)} \int\cdots\int_{\Lambda} \frac{z^N}{N!} \Delta(x_1,\ldots,x_N)\, e^{-\beta U(x_1,\ldots,x_N)} dx_1 \ldots dx_N$$

$$\times \left\{ \sum_{i=1}^{\infty} \frac{z^i}{i!} \int\cdots\int_{\Lambda} e^{-\beta U(x,\ldots)} h(X_j; X_i)\, dX_j \right. \qquad (III.24)$$

The $h(X_j; X_i) = h(x_1,\ldots,x_j, x_{j+1},\ldots,x_i)$ tell us that the expression in brackets is the partition function for the system enclosed in the volume Λ minus the volume occupied by the cluster which we shall denote by v_N (the N corresponding to the number of particles constituting the cluster). In other words, we are talking about $\Xi((\Lambda - v_N), z, \beta)$.

Eqn. (III.24) can now be written as

$$P_N = \left\{ \int\cdots\int_{\Lambda} \frac{z^N}{N!} \Delta(x_1,\ldots,x_N) e^{-\beta U(x_1,\ldots,x_N)} dX_N \right\} \times$$

$$\times \frac{\Xi((\Lambda - v_N), z, \beta)}{\Xi(\Lambda, z, \beta)}$$

The quotient $\dfrac{\Xi((\Lambda - v_N), z, \beta)}{\Xi(\Lambda, z, \beta)}$ equals the probability (in the grand canonical ensemble on Λ) that all the volume v_N is empty.

In order to obtain lower bounds similar to those by Lebowitz and Penrose[30] we subdivide the volume v_N into cubes with characteristic length α. This lenth can be taken as small as we please so that in the limit when the number of cubes tends to infinity α will tend to zero. The regions of v_N not contained in any of the cubes -near the borders of v_N - in this limit will also vanish.

As in the discrete case (where a lattice was used) we define a function η_i which for a given configuration takes on the value 1 if the cube $(v_N)_i$ contains particles and the value 0 if there are no particles inside $(v_N)_i$. In this case particles are taken as points and therefore situations where a particle falls in the frontier between two cubes will be highly improbable.

The characteristic function of the event that all the cubes contain no particles is $\prod_{i \in \bar{N}^{\mathcal{P}}} (1-\eta_i)$ where $\bar{N}^{\mathcal{P}} = \{1, 2, \ldots, N^{\mathcal{P}}\}$ and $N^{\mathcal{P}}$ is the number of cubes into which v_N was subdivided.

The probability that all the volume v_N is empty will be close to $\langle \prod_{i \in \bar{N}^{\mathcal{P}}} (1-\eta_i) \rangle$, and will be equal to the corresponding expression, when the limit $N^{\mathcal{P}} \to \infty$ is taken.

Since $$\prod_{i \in \bar{N}^{\mathcal{P}}} (1-\eta_i) \geq 1 - \sum_{i \in N^{\mathcal{P}}} \eta_i$$

then $$\langle \prod_{i \in \bar{N}^{\mathcal{P}}} (1-\eta_i) \rangle \geq 1 - \sum_{i \in \bar{N}^{\mathcal{P}}} \langle \eta_i \rangle \qquad (III.26)$$

and if we take the limit when $N \to \infty$ the Σ becomes an integral (in the sense of a Riemann integral), the volumes go to zero and the function η_i becomes a function of position $\eta(\vec{x})$ defined as

$$\eta(\vec{x}) = \begin{cases} 1 & \text{if threre is a particle at the point } \vec{x} \\ 0 & \text{if not} \end{cases}$$

Expression (III.26) takes the form

$$\lim_{N\to\infty} \langle \prod_{i \in N} (1-\eta_i) \rangle \geq \lim_{N\to\infty} (1 - \sum_{i \in N} \langle \eta_i \rangle) = 1 - \int_{v_N} \langle \eta(\vec{x}) \rangle \, d\vec{x}$$

$$= 1 - \int_{v_N} \rho(\vec{x}) \, d\vec{x}$$

since in this case $\langle \eta(\vec{x}) \rangle$ is the particle density.

Using this result in (III.25) we get

$$P_N \geq \left\{ \int \cdots \int_{\Lambda} \frac{Z^N}{N!} \Delta(x_1, \ldots, x_N) \, e^{-\beta U(x_1, \ldots, x_N)} \, d\vec{x}_N \right\} \times$$

$$\times \left(1 - \int_{v_N} \rho(\vec{x}) \, d\vec{x} \right)$$

If $\rho(\vec{x})$ is constant in v_N, $1 - \int_{v_N} \rho(\vec{x}) \, d\vec{x}$ becomes $(1 - \rho v_N)$. If $\rho(\vec{x})$ is not constant we can take $\rho_{max} = \max \{ \rho(\vec{x}) / \vec{x} \in v_N \}$ and therefore $1 - \int_{v_N} \rho(\vec{x}) \, d\vec{x} \geq 1 - \rho_{max} v_N$. Defining $\rho(\vec{x})$ as

$$\rho = \begin{cases} \rho & \text{if } \rho(x) \text{ is constant in } v_N \\ \rho_{max} & \text{if } \rho(x) \text{ is not constant in } v_N \end{cases}$$

we obtain for P_N

$$P_N \geq \left\{ \int \cdots \int_{\Lambda} \frac{Z^N}{N!} \Delta(x_1, \ldots, x_N) \, e^{-\beta U(x_1, \ldots, x_N)} \, d\vec{x}_N \right\} \times (1 - \rho v_N)$$

which is the same as

$$P_N \geq z^N Z_N (1 - v_N \rho) \qquad \text{III. 28}$$

That we can get a lower bound on m_N is a consequenc ob the above inequality; from the definition of m_N we see tl

$$m_N = \frac{1}{|\Lambda|} \sum_{\gamma : |\gamma| = N} P(\gamma) \geq \frac{1}{|\Lambda|} \sum_{\gamma : |\gamma| = N} z^N Z_N (1 - v_N \rho)$$

Proceeding again as in (III. 17) we obtain

$$m_N \geq (1 - v_N) \rho \sum_{\gamma : |\gamma| = N} z^N \frac{Z_N}{|\Lambda|} \qquad \text{(III. 29)}$$

so that by combining (III. 23) and (III. 29), m_N is shown to be bounded by

$$(1 - v_N \rho) \sum_{\gamma : |\gamma| = N} z^N \frac{Z_N}{|\Lambda|} \leq m_N \leq z^N Q_N$$

from where it follows that at low densities (z small enough) the expected number of N-particle clusters can be approximated by

$$m_N \approx z^N Q_N \qquad \text{(III. 30)}$$

which reproduces, for a continuous system, the approximation to m_N obtained by Penrose and Lebowitz[30] for a lattice gas.

THE REPLACEMENT FACTOR.

Let F_N stand for the internal free energy of a cluster of N particles. Then F_N and Q_N will be related by

$$Q_N = \exp\{-\beta F_N\}$$

and hence m_N can be expressed as

$$m_N \simeq \exp(-\beta F_N)$$

$$m_N \simeq \exp\{-\beta(F_N - NkT\log z)\} \qquad (III.31)$$

The quantity $F_N - \frac{N}{\beta}\log z$ can be interpreted as the free energy change occurring if N single-particle clusters are substituted by a N-particle cluster.

In nucleation theory the formula[73]

$$F_N = Nf + N^{(\nu-1)/\nu} S \qquad (III.32)$$

is accepted as a good approximation. In here f is the equilibrium bulk free energy per particle for the dense phase, S is proportional to the surface tension and ν is the number of dimensions .

Another formula normally used in nucleation theory is[82, 83]

$$m_N \simeq \Gamma m_1 e^{-W_N/kT} \qquad (III.33)$$

where m_N has the same meaning as before. W_N is defined by

$$W_N = N(\mu_d - \mu_v) + N^{(\nu-1)/\nu} s$$

with μ_d and μ_v the chemical potentials of the cluster and of the vapor. W_N can be seen as an approximation to the reversible work required to form an N-particle cluster. Γ stands for the "replacement factor"[82,83,84] which is a quantity introduced to allow "for the differences of definition between the partition function of a cluster on the one hand and a portion of bulk liquid on the other".

The use of these approximations has not been rigorously justified in general, most of the work having been done on discrete systems. Fisher and Caginalp[85] justified the use of (III.32) for the thermodynamic free energy of an N-particle system on a lattice with a number of sites increasing in proportion to N but this result was not carried on to include the case where F_N is the cluster free energy.

Penrose and Lebowitz made $\mu_\ell = f$ and $\mu_v = -\frac{\log z}{\beta}$ in the case of a lattice gas, this being an identification that seems natural. Using these inequalities and eqn. (III.34), m_N reads

$$m_N \simeq \Gamma m_1 \exp\{-\beta N(f + kT\log z) + N^{2/3}s\}$$

so that

$$m_N \simeq \Gamma m_1 z^N \exp\{-\beta(Nf + N^{2/3}s)\}$$

where ν was taken to be $\nu = 3$. Then they took the replace-

ment factor to be

$$\Gamma = m_1^{-1} \quad (\simeq z^{-1})$$

so that

$$m_N \simeq z^N \exp\{-\beta(Nf + N^{2/3}s\}$$

which happens to be the same as the approximation suggested by the rigorous theory if eqn. (III.32) is used in eqn. (III.31).

Looking back to the continuous model we recall the expression derived in (III.30) which formally looks identical to the analogous equation obtained in the discrete case (see Chapter II). Since the relation between Q_N and F_N is not based on the model being used therefore we can extend the validity of the approximation (III.31), namely

$$m_N \simeq \exp\{-\beta(F_N - NKT\log z)\}$$

to the continuous case under consideration.

Assuming the validity of eqn. (III.32), (III.33) and (III.34) we can combine them in exactly the same manner as before so that eqn. (III.35) is reproduced and once again, if we take Γ to be

$$\Gamma = m_1^{-1} \quad (\simeq z^{-1})$$

then

$$m_N \simeq z^N \exp\{-\beta(Nf + N^{2/3}s)\} \quad (III.36)$$

thus showing, in our state of knowledge, to what extent discrete and continuous cases can be compared.

A most wellcomed feature of this treatement is the fact that in both the discrete and the continuous cases the same approximation can be made, by means of assigning the same value to Γ, therefore giving support to the idea of identifying Γ and m_i^{-1}.

Unfortunately the rigorous theory for continuous systems is not well developed and much is still to be done in order to justify the use of the equations involved in obtaining expression (III.36).

CONCLUSIONS.

After all the material reviewed the impression is that a massive work remains to be done. The name metastability applies to a phenomenon which is not entirely covered in any of the descriptions developed so far. This fact is made patent in the separation into analytic and dynamic aspects of metastability carried out in the first two chapters. The authors treat different aspects of metastability and it is not obvious in general how the different problems arising in the description of metastable states can be included in the approaches described in this thesis.

The most complete works are those of Sewell and of Penrose and Lebowitz and they have proved to be fruitful in that many results have appeared afterwards bringing support to the ideas on which the works are based. Sewell relies heavily on the apparatus used in equilibrium statistical mechanics and on stability concepts; he introduces a classical model with a Van der Waals interaction in which the pressure for the metastable phase is the analytic continuation of the pressure for the stable phase. The presence of metastable states has been proved by the same author for the quantum case. But nevertheless in his approach he had to assume the existence of a suitable kinetic law governing the evolution in time of the system. On the other hand, Penrose and Lebowitz paid more attention to the kinetic aspects of metastability, and using their definition of what a metastable state is and the Becker-Döring set of equations they were able to provide upper bounds to the nucleation rate of clusters. If under ceratin values of the thermodynamic para-

meters the number of clusters of a ceratin size can be maintained for a certain amount of time then the nucleation rate will give a measure of the "slow process" by which the system escapes from the metastable state. A restriction to this and all the other approaches is that there is no clear distinction of the "degree of metastability" of the system and, particular to this approach there was the assumption of dealing with a system at low densities and temperatures.

In the last chapter I was able to show, under certain conditions, that the approximation for the number of clusters of size N obtained in a continuous model is formally the same as the one obtained by Penrose and Lebowitz for a lattice gas. This result makes more plausible the conjecture that, at least for small densities, the "replacement factor" can be approximated by the inverse of the number of clusters with just one particle. If we use this conjecture then the expression for m_N is in agreement with the results of nucleation theory.

APPENDIX A. A MARKOV PROCESS AND EVOLUTION IN TIME OF THE STATE OF THE SYSTEM.[21]

Essentially Holley studied a classical lattice system where at each site of the lattice we have a particle in the up or down direction. The evolution in time was through a Markov process which can be described as follows: if at time t the configuration is $\chi_\alpha(t)$ then the particle taken into consideration reverses its spin some time during $(t, t+\Delta t)$ with probability

$$\Delta t \exp(-\beta H) + o((\Delta t)^2)$$

where H is the energy of the system.

The main results obtained by Holley state that for all initial states the free energy is non-increasing and that it strictly decreases from any initial state which is shift invariant but not an equilibrium state. In addition the system converges weakly to the set of Gibbs distributions.

APPENDIX B. KMS STATES AND GIBBS STATES.[87]

A C*-dynamical system is a pair consisting of a C*-algebra $\mathcal{A}$ and a one-parameter group α_t , $t\in\mathbb{R}$ of automorphisms of $\mathcal{A}$ such that for each $a\in\mathcal{A}$, $\alpha_t a$ is continuous in $t\in\mathbb{R}$. In the following we assume that $\mathcal{A}$ is separable and unital ($1\in\mathcal{A}$).

A state φ of $\mathcal{A}$ is called an (α_t,β)-KMS state (or simply a KMS state) if it satisfies the following condition

For every pair of elements of a and b of $\mathcal{A}$, there exists a function $\mathcal{F}_{a,b}(z)$ of a complex variable z defined on the closed set

$$I_\beta \equiv \{z : Im\, z \in [0,\beta] \text{ or } [\beta,0]\}$$

such that

i) $\mathcal{F}_{a,b}(z)$ is bounded and continuous on I_β ,

ii) $\mathcal{F}_{a,b}(z)$ is holomorfic in the interior of I_β (this condition being empty for $\beta=0$)

iii) the boundary values are given by

$$\mathcal{F}_{a,b}(t)=\varphi(a\alpha_t b) \qquad \mathcal{F}_{a,b}(t+i\beta)=\varphi((\alpha_t b)a)$$

This condition was first introduced in quantum statistical mechanics by Kubo, Martin and Schwinger as a condition satisfied by thermodynamic Green's functions and was first formulated in C*-algebra lenguage by Haag, Hugenholtz and Winnink[26] who called it the Kubo-Martin-Schwinger boundary

condition.

In statistical mechanics, α_t describes the time development of the system and the KMS condition is considered to be a condition characterizing the state of the system at thermal (with the absolute temperature $T = 1/k\beta$ where k is the Blotzmann constant).

The importance of KMS states in relation to Gibbs states is seen in the following result:

If $\mathcal{A}$ is the algebra of all $n \times n$ matrices ($n < \infty$) then there exists $H \in \mathcal{A}$ such that $\alpha_t(a) = e^{itH} a e^{-itH}$, $a \in \mathcal{A}$. Then there is a unique (α_t, β)-KMS state and it is given by the following Gibbs state:

$$\varphi_\beta^G(a) = Tr(e^{-\beta H} a) / Tr(e^{-\beta H})$$

APPENDIX C. CLUSTER ESPANSION.[41]

The Mayer cluster expansion is a power series expressing the logarithm of the grand partition function for a finite volume Λ as a power series in the fugacity z .

Many systems of physical interest can be treated classically. A large class of such systems is described by a classical hamiltonian for N particles of the form

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} v_{ij}$$

where p_i is the momentum of the i-th particle and the potential of interaction between the i-th and the j-th particle is denoted by $v_{ij} = v(|\vec{r}_i - \vec{r}_j|)$. Let Q_N stand for the partition function for a system occupying a volume Λ . Hence

$$Q_N(\Lambda,\beta) = \frac{1}{N!\,h^{3N}} \int_{\Lambda} d^{3N}p\, d^{3N}r \; \exp\left(-\beta \sum_i \frac{p_i^2}{2m} - \beta \sum_{i<j} v_{ij}\right)$$

If we denote by $Z_N(\Lambda,\beta)$ the integral

$$Z_N(\Lambda,\beta) \equiv \int d^{3N}r \; \exp\left(-\beta \sum_{i<j} v_{ij}\right)$$

which is known as the configuration integral then $Q_N(\Lambda,\beta)$ can be expressed as

$$Q_N(\Lambda,\beta) = \frac{1}{N!\,\lambda^{3N}} Z_N(\Lambda,\beta)$$

where $\lambda = \sqrt{2\pi\hbar^2/mkT}$ is the thermal wavelength.

The grand partition function will now read

$$\Xi(\Lambda, z, \beta) = \sum_{N=0}^{\infty} \left(\frac{z}{\lambda^3}\right)^N \frac{Z_N(\Lambda, \beta)}{N!}$$

For potentials v_{ij} of a certain kind a method has been developed for the calculation for the configuration integral. This method consists in expanding the integrand in powers of $exp[(-\beta v_{ij}) - 1]$. This leads to the cluster expansion of Ursell and Mayer which, for a dilute gas, goes as follows: let $\int_{ij}$ be defined as

$$e^{-\beta v_{ij}} \equiv 1 + f_{ij}$$

so that now $Z_N(\Lambda, \beta)$ will appear as

$$Z_N(\Lambda, \beta) = \int_{\Lambda} d^{3N}r \prod_{i<j} (1 + f_{ij})$$

A convenient way to enumerate all the terms in the expansion is to associate each term with a graph. By a graph we will understand the following:

An N-particle graph is a collection of N distinct circles numbered 1,2,...,N, with any number of lines joining the same number of distinct pairs of circles. If the distinct pairs joined by lines are the pairs $\alpha, \beta, \gamma, \ldots, \lambda$, then the graph represents the term

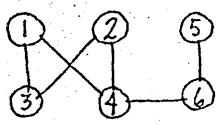
$$\int_{\Lambda} d^{3N}r \; f_\alpha f_\beta \ldots f_\lambda$$

appearing in the expansion C.1.

With such a convention we can state that

$$Z_N(\Lambda,\beta) = \text{(sum of all distinct N-particle graphs)}$$

We define an ℓ-cluster to be an ℓ-particle graph in which every circle is attached to at least one line and every circle is joined directly or indirectly to all other circles. For example



$$= \int d^3r_1 \ldots d^3r_6 \; f_{12} f_{23} f_{14} f_{46} f_{56}$$

We define a cluster integral $b_\ell(\Lambda,\beta)$ by

$$b_\ell(\Lambda,\beta) = \frac{1}{\ell!\,\lambda^{3\ell-3}\Lambda}\,(\text{sum of all possible } \ell\text{-clusters})$$

In terms of $b_\ell(\Lambda,\beta)$ we obtain that

$$Q_N(\Lambda,\beta) = \sum_{\{m_\ell\}} \prod_{\ell=1}^{N} \frac{1}{m_\ell!} \left(\frac{V}{\lambda^3} b_\ell\right)^{m_\ell}$$

with m_ℓ being the number of ℓ-clusters; finally

$$\Xi(\Lambda,z,\beta) = \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \cdots \left[\frac{1}{m_1!}\left(\frac{V}{\lambda^3} z b_1\right)^{m_1} \frac{1}{m_2!}\left(\frac{V}{\lambda^3} z^2 b_2\right)^{m_2} \cdots\right]$$

and therefore

$$\frac{1}{V}\log \Xi(\Lambda,z,\beta) = \frac{1}{\lambda^3} \sum_{\ell=1}^{\infty} b_\ell z^\ell$$

from which we obtain the equation of state in parametric form

$$\frac{P}{kT} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l$$

$$\frac{1}{v} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} l\, b_l z^l$$

with $v = V/N$

This is known as the cluster expansion for the equation of state.

APPENDIX D. THE KIRKWOOD-SALSBURG EQUATIONS.[15]

The Kirkwood-Salsburg equations form a linear inhomogeneous system satisfied by the correlation functions $f_\Lambda(x)_n$ where $f_\Lambda(x)_n = f_\Lambda(x_1, \dots, x_n)$ and Λ is the volume occupied by the system. The utility of these equations is that they provide a powerful tool for the study of the correlation functions at small activity. The K-S equations are expressed as

$$f_\Lambda(x)_1 = \chi_\Lambda(x)_1 \, z \left[1 + \sum \frac{1}{n!} \int dy_1 \dots dy_n \; k(x_1, (y)_n) \, f_\Lambda(y)_n\right]$$

$$f_\Lambda(x)_m = \chi_\Lambda(x)_m \, z \, \exp\left[-\beta W'(x)_m\right] \times$$

$$\times \, f_\Lambda(x)'_{m-1} + \sum_{n=1}^{\infty} \frac{1}{n!} \int dy_1 \dots dy_n \; k(x_1, (y)_n) \, f_\Lambda((x)'_{m-1}, (y)_n)\Big]$$

where χ_Λ is the characteristic function for the region Λ and

$$W'(x)_m = \sum_{i=2}^{m} \Phi(x_i - x_1)$$

with $\Phi(x_i - x_1)$ the interaction potential between particles i and 1. $(x)'_{m-1}$ stands for $(x)'_{m-1} = (x_2, \dots, x_m)$.

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